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FINAL REPORT
CHEMICAL PUMP STUDY
FOR
PIONEER VENUS PROGRAM

By Mary Rotheram

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Moffett Field, Calif. 94035

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FINAL REPORT

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SUMMARY

Two chemical pumps were designed for the Pioneer Venus large probe mass spectrometer. Factors involved in the design selection are reviewed. One pump is designed to process a sample of the Venus atmosphere to remove the major component, carbon dioxide, so that the minor, inert components may be measured with greater sensitivity. The other pump is designed to promote flow of atmospheric gas through a pressure reduction inlet system. This pump, located downstream from the mass spectrometer sampling point, provides the pressure differential required for flow through the inlet system.

Both pumps utilize the reaction of carbon dioxide with lithium hydroxide. The available data for this reaction was reviewed with respect to the proposed applications, and certain deficiencies in reaction rate data at higher carbon dioxide pressures noted.

The chemical pump designed for the inert gas experiment has an estimated volume of 30 cm³ and weight of 80 grams, exclusive of the four valves required for the operation. This volume can be reduced if testing should demonstrate that the carbon dioxide reaction proceeds satisfactorily at pressures in excess of 100 mbar, the highest pressure for which data is available, or if a lower sensitivity or accuracy for the inert gas measurement is acceptable. The present design is based on a maximum inert gas content of two percent in the Venus atmosphere, and an error of less than five percent due to flow rate change during the mass scan. The impact of changing these values is discussed.

The chemical pump for the pressure reduction inlet system is designed for a total sample of 0.3 bar liter during the Venus descent. The pump is designed to interface with the inlet system through a long capillary to minimize back diffusion of the inert gases and water vapor which is in

equilibrium with the lithium hydroxide hydrate produced by the reaction. Depending on the mode of operation of the inlet system, back diffusion can be minimized to the point where it should not interfere with the analysis of the incoming sample gas. The pump designed for 0.3 bar liter sample has an estimated volume of 240 cm^3 and weighs approximately 200 grams. The size of this system can be reduced by using a smaller total sample. The present sample represents a ratio of $10^4:1$ for sample bypassed to that entering the mass spectrometer. It is believed that a ratio of $10^2:1$ could be utilized with a reduction in the pump size by a factor of 10.

The pump designs proposed are tentative since goals for accuracy and sensitivity for the experiments are not currently defined. Limited data on the rate of reaction under conditions applicable to these pumps is a restriction on optimizing the system designs. Fabrication and test plans for the pump designs for these plans are presented.

INTRODUCTION

A study program was undertaken to design two chemical pumps for the Venus Pioneer large probe mass spectrometer^{1,2,3} to determine the composition of the Venus atmosphere from an altitude of approximately 70 kilometers to the surface. The chemical pumps serve two purposes. One is a reactor unit which removes the major constituent of the Venus atmosphere, carbon dioxide, so that the minor, inert constituents can be analyzed more accurately by the mass spectrometer. The minor constituents of particular interest are helium, neon, argon, krypton, xenon and nitrogen. The amounts of these constituents are important in understanding the evolution of the planet. The second chemical pump is used in an inlet system designed to furnish a sample of the Venus atmosphere at reduced pressure to the mass spectrometer intake leak. By reacting with the major component of the atmosphere, this pump provides the pressure differential required for flow through the inlet system. The two systems are shown schematically in Figures 1 and 2.

The inert gas experiment sample will be taken during the initial part of the probe descent through the lower atmosphere. An intake line to the chemical pump will be opened and the atmospheric gas will flow into a gas volume or sample reservoir as shown in Figure 1. When a preselected pressure is reached, a valve will close, isolating a fixed amount of gas for

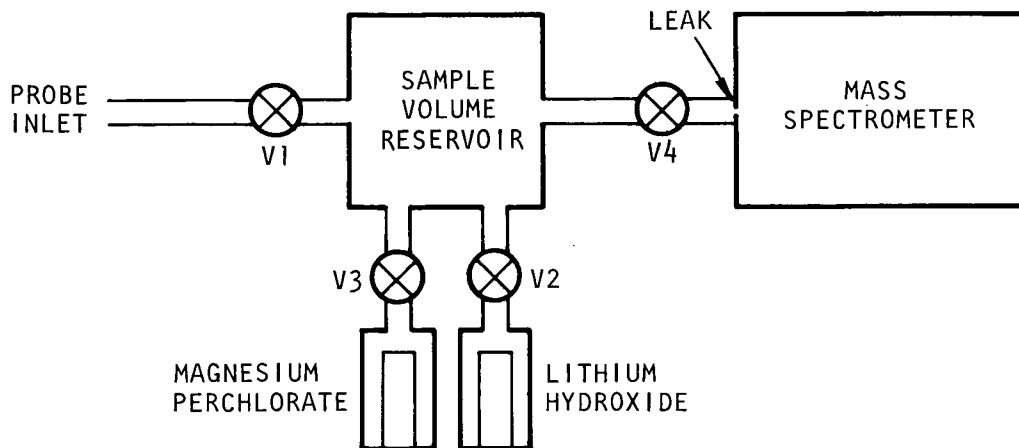


FIGURE 1.- Schematic of Chemical Pump for Inert Gas Experiment

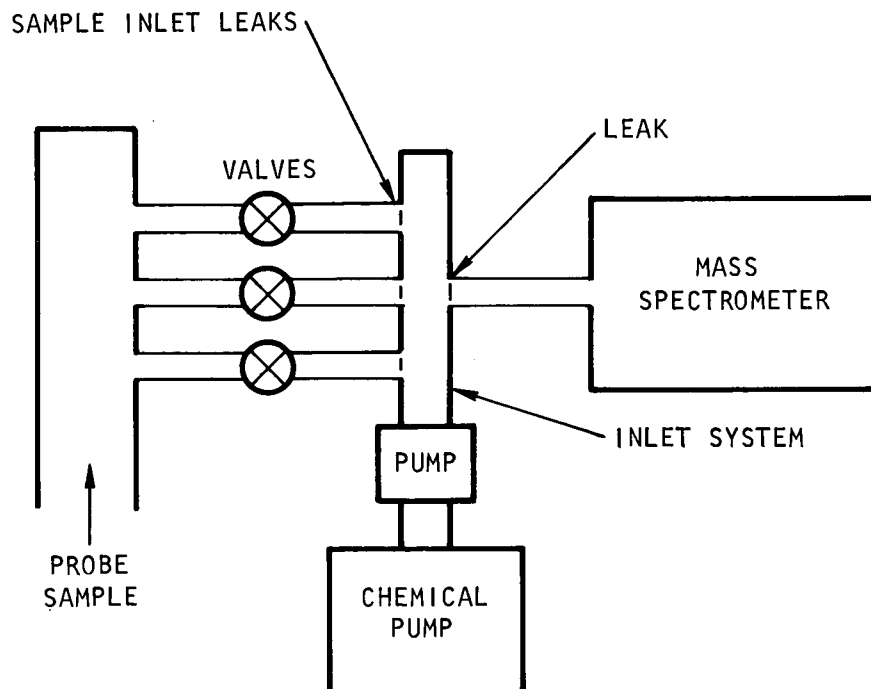


FIGURE 2.- Schematic of Chemical Pump for Ballast Volume Replacement

analysis. This sample will be processed to remove all gases except the inerts. At the end of the processing interval, a valve will be opened to admit the residual gas to the mass spectrometer for analysis. The factors to be established in designing the pump are the amount of gas to be processed, the time period for processing, the leak rate to the mass spectrometer, and the amounts of chemicals and configuration of system.

The dynamic chemical pump (ballast volume replacement) is part of an inlet system designed to provide a continuous flow of atmospheric gas at reduced pressure past the intake leak to the mass spectrometer. Direct sampling to the mass spectrometer over the pressure range involved in the probe descent (29 mbar to 95 bars) is technically difficult. Leaks or flow restrictors which will be molecular at pressures in excess of a few bars are not presently available. Therefore, a pressure reducing inlet system of the type shown schematically in Figure 2 has been proposed for sampling the Venus atmosphere. In this type of system, pressure at the intake leak of the mass spectrometer is controlled by the flow rate through the atmospheric leaks and the speed of the pump. The system is basically similar to a pressure reducing capillary system frequently used with laboratory mass spectrometers; the major difference lies in the variation of the sampling point pressure. In the system shown schematically in Figure 2, three leaks are used to control the flow rate, and consequently, the pressure at the mass spectrometer leak, of the Venus atmosphere gases. As the probe enters the atmosphere ($p \approx 29$ mbar) all three leaks are open. During descent, two of the leaks are closed sequentially, so that as the pressure increases, there are three repeated cycles of flow rate variation. In the conceptual design of the inlet system, an evacuated three liter reservoir was proposed to furnish the pressure differential required for flow through the system; however, this would occupy a relatively large volume inside the probe. The chemical pump serves the same purpose by removing the gas by chemical reaction, and would occupy a much smaller volume.

The reaction of carbon dioxide with lithium hydroxide has been used for controlling the carbon dioxide content in confined atmospheres (spacecraft, submarines, etc.), and in the Atmospheric Filter Assembly for the Mars Viking Lander mass spectrometer. The Atmospheric Filter Assembly application is similar in purpose to the chemical pump for the inert gas experiment for the Venus Pioneer mission.

In designing these chemical pump systems, certain assumptions have been made about the composition of the Venus atmosphere, the mission parameters, and the interface between the pump and other parts of the mass spectrometer system and the probe. Since this mission is still in the

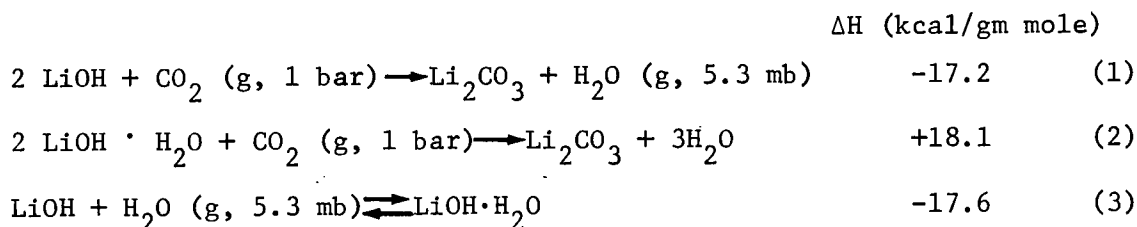
planning stage, some effort has been made to point out the effects of parameter changes on system design. One of the most critical parameters to the design of the chemical pump systems is the time rate of descent through the atmosphere, since both pumps are based on chemical reactions which have certain finite rate constants. Another critical factor is that the volume of the system should be minimal for the Venus mission. Weight is also a consideration as it is for all flight hardware.

CHEMISTRY

The proposed chemical pumps are based on the reaction of lithium hydroxide with carbon dioxide. The objective in the inert gas experiment is to obtain a measure of the nitrogen and noble gas content of the Venus atmosphere and to determine the ratios of the noble gas isotopes. Removal of carbon dioxide provides a sample enrichment which permits these measurements to be made more accurately. It also minimizes the interference in the nitrogen determination due to the carbon monoxide fragment ion and in the mass 22 neon isotope, due to doubly charged carbon dioxide ion. To obtain maximum sample enrichment, water vapor which is formed in the reaction of carbon dioxide must also be removed. Furthermore, although the carbon monoxide content of the atmosphere is presently believed to be less than $10^{-2}\%$ (see Table 1) it would be advantageous to provide for its removal in case higher than anticipated concentration is encountered.

Lithium Hydroxide Reaction

Lithium hydroxide is used as a scrubber for carbon dioxide in several applications, in manned spacecraft, submarines and deep submergence vessels to control the carbon dioxide content of the atmosphere. More recently, it is used in the atmospheric filter system of the Mars Viking Lander mass spectrometer, where it performs essentially the same function as that proposed for the Venus Pioneer inert gas chemical pump. Reaction rates have been measured in both types of systems, but the kinetics of the overall reaction are not well defined. In studies with atmospheric gases, the rate of reaction apparently depends on the presence of water but when pure carbon dioxide is used, the reaction apparently proceeds rapidly, even in the absence of water. The reactions involved are formally written as follows.



In the Viking studies, lithium oxide has also been used to replace part of the lithium hydroxide, in which case two additional reactions may be considered:



In studies related to control of the carbon dioxide content of confined atmospheres,⁴ it was demonstrated that reaction (1) did not occur in tests in which air containing carbon dioxide at a concentration of 300 parts per million was passed through a 3.2 g bed of lithium hydroxide at a flow rate of 300 cm³ per minute. However, when water vapor was present in the air stream, lithium hydroxide reacted with carbon dioxide at efficiencies depending on the relative humidity of the air. Highest efficiency was obtained when the water vapor content was a little higher than the equilibrium vapor pressure for the hydrate (reaction (3)). Under these conditions, the water formed apparently reacts to form the hydrate in a zone just ahead of the carbon dioxide reaction zone. At higher relative humidities, water fills the pores of the lithium hydroxide faster than carbon dioxide can react (at 300 ppm in air at 300 cm³/min) and lithium hydroxide utilization is less efficient. Lower relative humidities (less than the equilibrium vapor pressure of the hydrate) result in lower efficiencies for removal of carbon dioxide since the hydrate is not formed, and any hydrate present is dehydrated.

In these studies, the carbon dioxide content was relatively low and the heat generated by the reaction was small. At higher carbon dioxide concentrations, thermal effects become significant and rate measurements in flowing systems under these conditions become difficult. Some work has been performed in this area but results were not reported.⁵ Cyclical effects have been observed in atmospheric purification systems; the carbon dioxide reaction (in humid air) proceeds rapidly enough to raise the temperature of the lithium hydroxide bed, decomposing the hydrate and causing the reaction to stop.

TABLE 1.-
Composition of the Venus Atmosphere²

Component	Estimated Per Cent by Volume
CO ₂	97, + 3, -4
N ₂ , A & Inerts	< 2
O ₂	< 10 ⁻³
H ₂ O	$\begin{cases} 10^{-3} & 10^{-1} \\ 10^{-4} & 10^{-2} \end{cases}$
HCl	10 ^{-4.2}
HF	10 ^{-6.2}
CH ₄	< 10 ⁻⁴
CO	10 ^{-2.34}
COS	< 10 ⁻⁶ - 10 ⁻⁴
NH ₃	< 10 ^{-5.5}
N ₂ O	< 5 X 10 ⁻⁵
He	≈ 10 ⁻²
CH ₃ Cl	< 10 ⁻⁴
C ₂ H ₂	< 10 ⁻⁴
HCN	< 10 ⁻⁴
O ₃	< 10 ⁻⁶
C ₃ O ₂	< 10 ^{-4.3}
H ₂ S	< 10 ^{-1.7}
SO ₂	< 10 ^{-5.5}
CH ₃ F	< 10 ⁻⁴

As the bed of lithium hydroxide cools, the hydrate reforms when the water vapor pressure is higher than the hydrate equilibrium value and the reaction with carbon dioxide resumes.

Data from the Viking studies^{6, 7} were obtained under conditions similar to those which apply to the inert gas experiment, that is, in a static system with 90% carbon dioxide, which is presumably dry. The early experiments performed in a glass laboratory system gave time constants for the reaction of 20 seconds, corresponding to a reaction rate (first order kinetics) of 4 cm³/seconds. Carbon dioxide pressure of 10 torr were reduced to 5×10^{-3} torr in the 15 minutes allowed for the reaction. The reactant was a mixture of lithium hydroxide and lithium oxide. The most recent results⁶ in the Atmospheric Filter Assembly designed for the Mars mission indicate rapid reaction takes place at 20 mbar and 50°C (125°F) with a mixture of anhydrous lithium hydroxide and lithium oxide. Subsequent charges of carbon dioxide also react rapidly; the data do not indicate clearly whether or not some of the hydrate was present. Time constants measured in this system are of the order of 35 seconds at 23°C (73°F), corresponding to rate constants of 0.28 cm³/sec. At higher temperatures, time constants are somewhat longer (two experiments give values of 100 and 50 seconds). When the monohydrate is tested, the first charge of carbon dioxide reacts about as rapidly as with the anhydrous material, but subsequent charges react more slowly.

In these experiments with the Mars Atmospheric Filter Assembly, the carbon dioxide in the sample reservoir must pass through the small flight type valves to enter the lithium hydroxide chamber. The diffusive conductance of this valve has been estimated⁸ and it appears that the measured rate constants are about the value that would be expected for a reaction limited by diffusion through the valve. Changes in rates observed during the reaction could be attributed to changes in diffusion constants with pressure rather than changes in reaction rates. The slower rates observed in the experiment with the monohydrate may be attributable to the effect of water vapor pressure (in excess of the equilibrium value) on the diffusion constant. When two micron screens are placed over the valve port, the rates decrease by about a factor of two. It seems reasonably certain that the rates measured in the Atmosphere Filter Assembly are controlled by diffusion rates through the valve.

In a static system, starting with anhydrous lithium hydroxide, and assuming the reaction occurs, water vapor will be produced until the vapor equilibrium pressure of the hydrate is attained. At 25°C, this is approximately 5.3 mbar. Figure 3 shows the vapor pressure of the hydrate as a function of temperature. Once the equilibrium vapor pressure is reached,

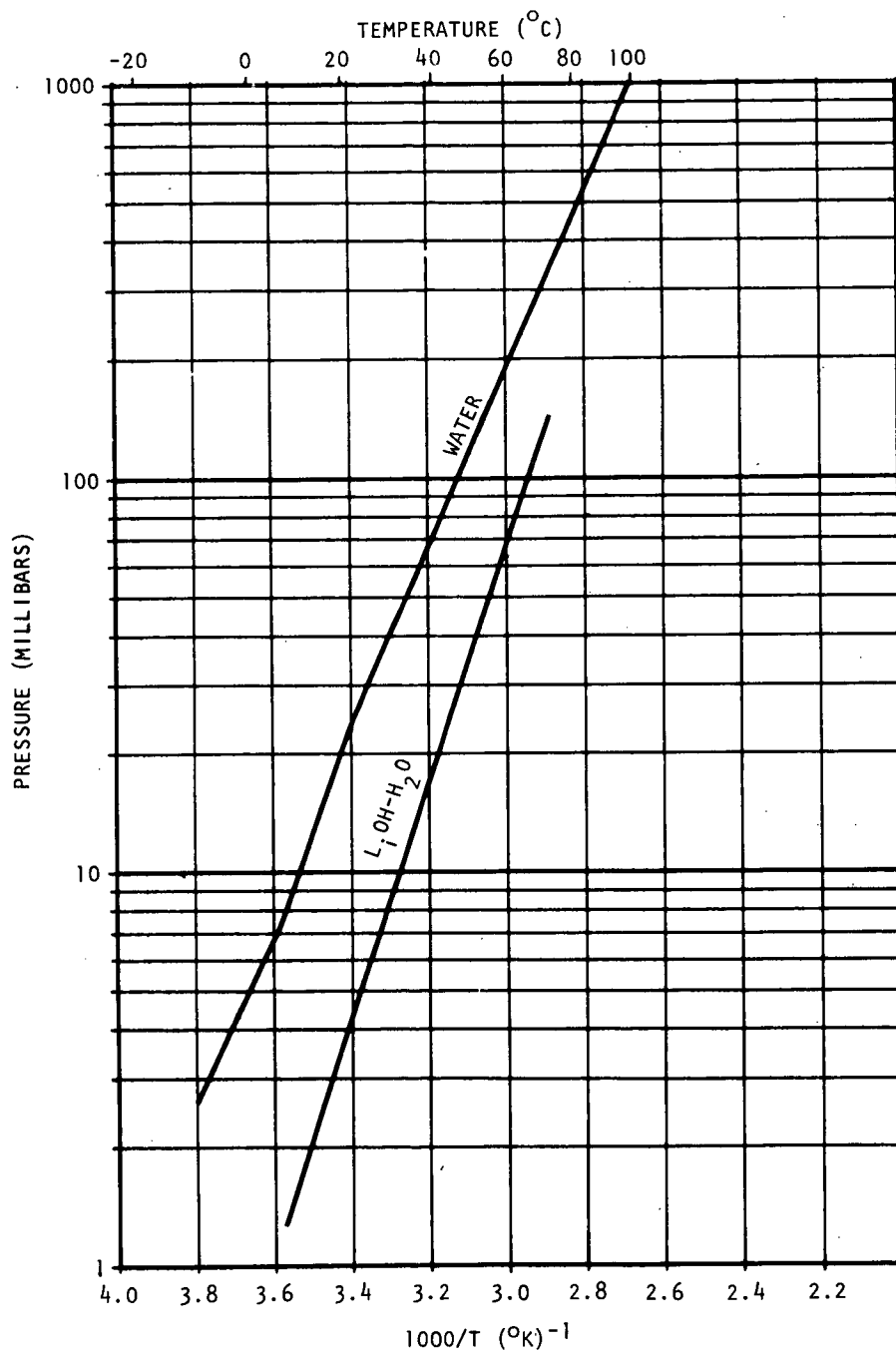


FIGURE 3.- Vapor Pressure of Water and Lithium Hydroxide Hydrate

the hydrate will form, and will continue to form until the available lithium hydroxide is converted to the hydrate, at which point the water vapor pressure will increase, possibly up to the saturation pressure.

If the observations made with carbon dioxide at 300 ppm in air apply equally well to pure carbon dioxide, the reaction rate with the hydrate should be much faster than with the anhydrous material. Depending on the volume of the system, and the initial pressure of carbon dioxide, there should be a change in rate during the reaction. However, this cannot be demonstrated from the available data because of the diffusion effects.

Lithium oxide in these experiments conserves weight in the system by allowing the water left in the lithium hydroxide chamber to react with the lithium oxide to form lithium hydroxide. The rate of this reaction is not known; it has been demonstrated⁷ that carbon dioxide does not react with lithium oxide. The use of lithium oxide for the Mars experiments is reasonable since a large number of determinations of the inert gas content is planned. For the Venus experiment in which only a single measurement can be made and the reaction time period is limited, however, it is better to use the most reactive form of lithium hydroxide.

Heats of reaction at 25°C estimated for the reactions are shown with the equations. The net reaction is exothermic as long as the hydrate is formed. If the heat generated by the reaction is absorbed in the lithium hydroxide, the temperature will increase, and the rate of formation of the hydrate will be slower. In a static system in which the only water available is that produced by the carbon dioxide reaction, the reaction should proceed at some steady rate which depends on the rate of heat transfer from the lithium hydroxide. Conceivably, the temperature of the lithium hydroxide might be high enough that the equilibrium vapor pressure of water would be higher than the saturation vapor pressure at some other, cooler part of the system. In this case water might separate as a liquid which could plug small passages in the system. In some experiments reported in the preliminary Viking experiment,⁷ pressures of 100 torr carbon dioxide were employed, apparently without difficulty, although the rate constants appear to be lower than those measured for 10 torr starting pressure.

Other acidic components of the Venus atmosphere are also expected to react with lithium hydroxide. These components include the hydrogen halides, hydrogen sulfide, hydrogen cyanide, and sulfur dioxide. The concentrations of these components in the atmosphere are believed to be quite low, however, and they are not expected to interfere with the reaction of carbon dioxide with lithium hydroxide.

For the Venus Pioneer inert gas experiment, the most critical area for investigation is the reaction rate dependence on initial carbon dioxide pressure; the fate of water in the system should also be investigated. At present, the rates of these reactions at pressures and temperatures in the range applicable for this experiment are not known well enough to predict what effects will be observed. It would be advantageous, however, to sample at relatively low pressures consistent with keeping a minimum volume system.

Carbon Monoxide

The carbon monoxide content of the Venus atmosphere is expected to be relatively low, less than 0.01 volume percent. Nevertheless, since it is of interest to measure nitrogen at concentrations which may also be very low, silver oxide will be included in the chemical pump for the inert gas experiments to minimize any interference in the analysis for nitrogen.

Data from the Viking program indicates that carbon monoxide at pressures of the order of two mbar is reduced to less than one percent of the original value in about 12 minutes concurrently with the reaction to remove carbon dioxide.⁶ At very low pressures such as that expected in the Venus atmosphere, the reaction might be somewhat slower. Higher carbon dioxide pressures might also interfere with the reaction. At present, it does not appear advantageous to base the system design on rates of reaction which might be involved for such a minor constituent of the atmosphere.

Water Sorption

Magnesium perchlorate is used to sorb the water vapor remaining in the sample volume after the lithium hydroxide reaction is complete. The vapor pressure of water in equilibrium with lithium hydroxide hydrate is of the same order of magnitude as the pressure expected from the inert gases. Its removal will increase the sensitivity for the inert gas analysis. Magnesium perchlorate forms a dihydrate and a hexahydrate. The vapor pressure of the dihydrate is shown in Figure 4.⁸ Measurements in the Mars Atmospheric Filter system show that approximately the same time period is required for this step as for the reaction of carbon dioxide with lithium hydroxide. Water vapor pressures of the order of 10^{-4} mbar were reached in the preliminary Viking experiments.

Most of the preceding discussion is related to the inert gas experiment. Rates are also critical for the chemical pump for ballast volume replacement. For this experiment only the reaction of carbon dioxide with

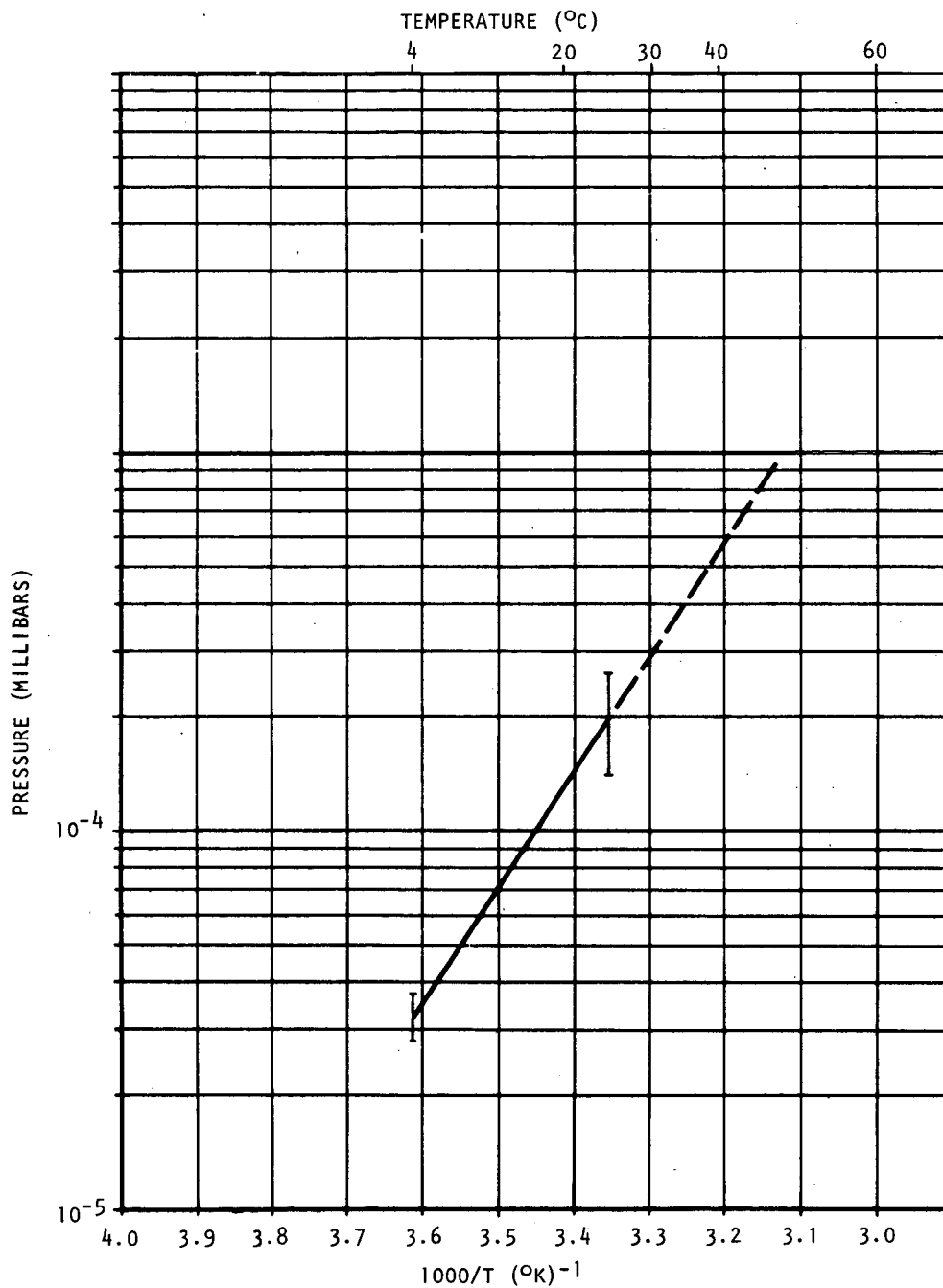


FIGURE 4.- Magnesium Perchlorate Estimate of the Vapor Pressure of the Dihydrate

lithium hydroxide is considered necessary, although provision could be made to pump carbon monoxide as well if this should prove to be a significant portion of the Venus atmosphere.

Summary

In summary, it appears that the reaction of carbon dioxide with lithium hydroxide can be used satisfactorily in the proposed chemical pumps for the Venus experiments. The rates of the reaction should be high enough that the experimental objectives can be accomplished within the descent time period. The lack of data or complete understanding of the rates of reaction at higher pressures forms one limitation on design of the inert gas experimental pump.

It would be advantageous to have reaction rate data at higher pressures. This data may be obtained in engineering evaluation systems resembling a final design quite closely because thermal effects and conductance limitations, both of which may be important factors in determining rates, are dependent on the system geometry. Certain points might be resolved in laboratory system tests. One is the requirement for the presence of the hydrate for the reaction with pure carbon dioxide. If the reaction is fast with the anhydrous material, a certain amount of processing could be eliminated in preparation of the lithium hydroxide. However, most evidence is contrary to this. A second point of interest is the relative rates of hydrate formation and carbon dioxide reaction. The rate of hydrate formation must be fast enough to keep pace with the carbon dioxide reaction or, with high pressures of carbon dioxide, water might be formed in excess of the saturation vapor pressure. If it is assumed that reaction of carbon dioxide occurs only with the hydrate, this possibility does not seem very likely. These points could be established fairly simply in a laboratory system.

CHEMICAL PUMP DESIGN ANALYSES

Chemical Pump for the Inert Gas Experiment

The purpose of this experiment is to provide a carbon dioxide free sample of the inert gases for analysis by the mass spectrometer. If the carbon dioxide is removed from a sample of the Venus atmosphere, the residual gases can be examined more accurately with the mass spectrometer since

they can be introduced into the ion source at a much higher partial pressure than would be possible in the presence of a bulk constituent such as carbon dioxide. There is considerable interest in determining the isotope ratios for the inert gases to establish the age of the planet. A factor of 50 improvement in sensitivity which can be obtained with an inert gas chemical pump designed for a two percent concentration of inerts in the atmosphere. For argon at an atmosphere concentration of 100 ppm ($10^{-2}\%$), the ^{36}Ar concentration in the mass spectrometer ion source would be 2.2×10^{-9} mbar for the sample from the chemical pump in comparison to 4.4×10^{-11} mbar for an unprocessed sample of the atmosphere, assuming earth normal abundances.

Furthermore, if carbon dioxide and carbon monoxide are removed from the sample prior to the analysis, a much more accurate analysis for nitrogen can be obtained. Flight mass spectrometers do not have sufficient resolving power to permit identification of the N_2^+ ion in the presence of CO^+ from carbon dioxide ($\text{CO}_2^+ \rightarrow \text{CO}^+ + \text{O}$) or carbon monoxide. While the fragmentation ratios for this reaction are usually determined for a particular instrument and are reasonably stable, the accuracy of determination of small amounts of nitrogen in the presence of large amounts of carbon dioxide is limited by the shot noise levels associated with the large ion current at mass 28. Under these conditions, too, it is generally not feasible to distinguish carbon monoxide from nitrogen by measuring the mass 12 ion current because of the large contribution from carbon dioxide. Even in the absence of carbon dioxide, the mass 12 ion current is of limited reliability for carbon monoxide determination since most mass spectrometers have significant background levels of mass 12 from organics used in cleaning processes. Therefore, the best determination of the nitrogen content can be obtained by removing carbon dioxide and carbon monoxide before admitting the sample to the mass spectrometer. The chemical pump for the inert gas experiment is designed for this purpose.

The design analysis of this pump begins with a consideration of the amount of gas sample which must be processed to obtain a sample for the mass spectrometer. This involves some assumptions about the composition of the Venus atmosphere and the flight mass spectrometer characteristics. Once the sample size has been established, the pressure at which the sample is taken must be chosen. The sample reservoir volume can be minimized by selecting a high pressure sample. However, such a selection shortens the time period available for processing the sample. The impact of initially high pressures in the reaction rate of carbon dioxide with lithium hydroxide cannot be established conclusively from the existing data. Since the time factor is relatively critical and the minimum volume constraint is important, it is essential to perform some preliminary laboratory experiments to

establish the pressure, temperature and reaction rate characteristics over a reasonable range of these variables for the Venus mission.

Operation. - Chemical pump operation for the inert gas experiment is reviewed briefly to provide a basis for detailed design consideration. It is proposed in this experiment to take in a fixed amount of the Venus atmosphere and process it to remove carbon dioxide. A schematic of this system is shown in Figure 1. The amount of sample gas is determined by the volume of the sample reservoir and the pressure in the Venus atmosphere at which the sampling period is terminated. Figure 5 shows the atmospheric pressure as a function of time for a typical descent through the Venus atmosphere. A valve connecting the lithium hydroxide chamber to the sample reservoir is opened and the sample is processed to remove carbon dioxide. After the appropriate time interval to remove the carbon dioxide (and carbon monoxide), this valve is closed and a second valve opened to expose the residual gas sample to magnesium perchlorate which is used to remove water vapor. At the end of the water removal cycle, this valve is closed and valve four opened to admit residual gases to the mass spectrometer through a relatively high conductance leak. Some time prior to admission of the residual gas sample to the mass spectrometer, the direct atmospheric sample line must be closed off, and, if time permits, the background in the mass spectrometer should be scanned. Exact details of these operational sequences have not been established at the present time. After the mass analysis of the residual gases, valve four is closed. The gas trapped between the leak and valve four must be pumped out through the mass spectrometer before accurate compositional analysis can be resumed in the atmospheric sampling line.

Sample pressure volume relationship. - Design of the chemical pump for the inert gas analysis must provide a sufficient sample so that the flow rate through the mass spectrometer does not drop substantially during the mass scan. The amount of sample required depends on the allowable flow rate change, the time required for a mass scan, and the mass spectrometer operating conditions. For typical flight mass spectrometers, the maximum flow rate through the source is of the order of 6.7×10^{-3} mbar cm^3/sec . Mass spectrometer design considerations involved in flow rate limitations are discussed in the Appendix.

For optimum sensitivity, the inlet system must be designed to furnish a flow rate approaching the maximum value from the highest anticipated concentration of residuals in the atmosphere. For the Venus atmosphere, the nominal residual concentration is expected to be of the order of two percent or less. Conservatively, the system could be designed for a value

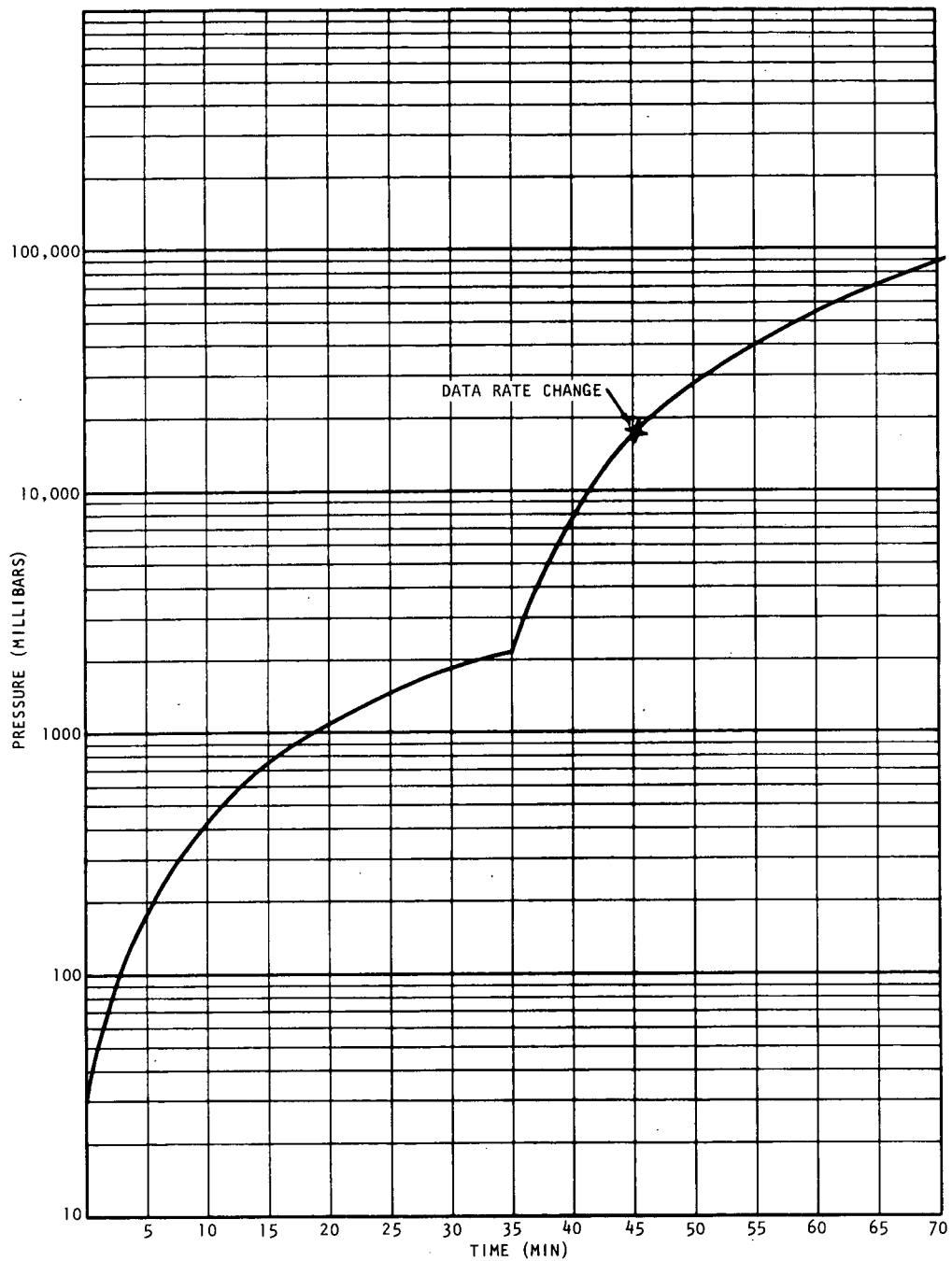


FIGURE 5.- Pressure as a Function of Time for Typical Venus Probe Descent Profile

somewhat higher than this, perhaps of the order of three to four percent. Ideally, the amount of sample taken should be large enough to furnish a flow rate of residuals which is constant or nearly constant over the time period involved in the scan at a value near the maximum allowable flow rate for the particular mass spectrometer.

The pressure change or the flow rate out of a reservoir is given by the following equation:

$$-V_i \frac{dp_i}{dt} = c_L (p_i - p_s)$$

where

v_i = volume of the inlet system sample reservoir

c_1 = conductance of the leak to the mass spectrometer

p_i = pressure in the inlet system sample reservoir

p_s = pressure in the mass spectrometer ion source

t = time

For $p_s \ll p_i$

the flow may be approximated by

$$Q = -V_i \frac{dp_i}{dt} = c_1 p_i$$

For a constant volume system, the change in flow rate is proportional to the change in pressure and, defining E as the allowable error due to change in flow rate during the scan time, t_s ,

$$E = \frac{\Delta Q}{Q} = \frac{\Delta P}{P}$$

$$\frac{1}{1 - E} = \exp (c_1 t_s / V_i)$$

The conductance of the leak c_1 is sized for maximum flow rate at the initial ($t = 0$) pressure of inerts

$$c_1 = Q/p_{i,o}$$

and

$$\frac{1}{1-E} = \exp \left(\frac{Q_{\max} t_s}{p_{i,o} V_i} \right)$$

The value of $p_{i,o}$ is related to the atmospheric pressure at which the sample is taken by

$$p_{i,o} = X_R P_A$$

where

X_R = design value for the mole fraction of inerts in the atmosphere

and

P_A = atmospheric pressure at the time the sample is taken.

The conductance of the leak for the mass spectrometer is given by

$$c_1 = \frac{Q_{\max} \text{ m.s.}}{X_R P_A}$$

Values of the sampling pressure required for different sample reservoir volumes are shown in Figure 6 for three design values of the mole fraction of inert gases and for selected value of E .

The requirement of flow stability, that is, the value chosen for Q , depends on the information desired from the experiment. If, for example, the ratio of two gases at the extremes of the mass range is of interest, a low value of E is necessary. If the ratio of isotopes of a single gas is the prime concern, a larger value for E can be accepted.

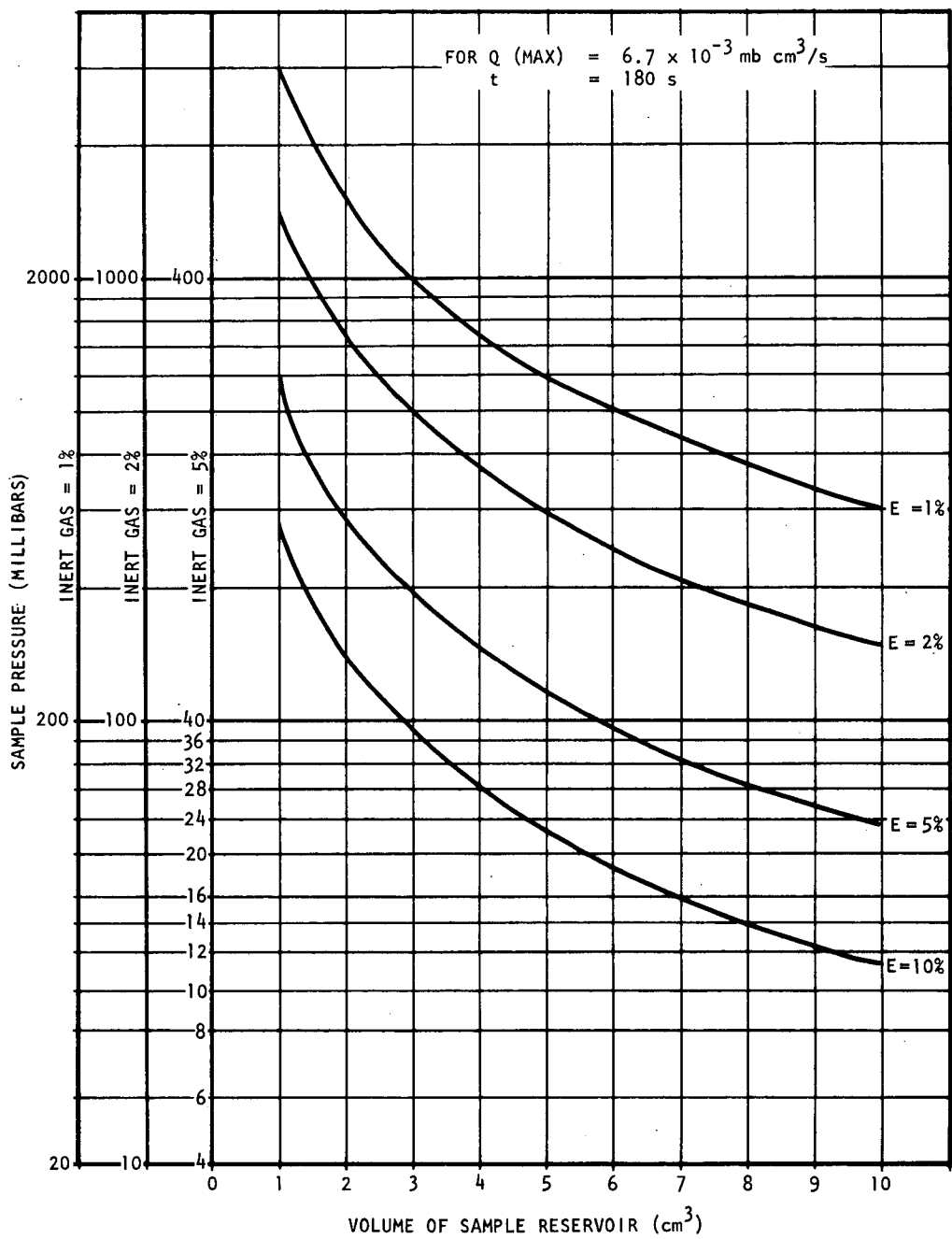


FIGURE 6.- Sample Pressure - Sample Volume Requirements

For defined experiment goals, the choice of a sample volume to minimize the total system volume implies a certain pressure for the sample. Higher pressure samples are obtained at lower altitudes. The time available for processing the sample is shortened since the sample is taken at a later time in the descent. The factors involved are considered in the section entitled "Carbon dioxide reaction."

Sensitivity - minimum detectable levels. - The minimum detectable levels for individual gases are primarily determined by the mass spectrometer design and operating conditions. The minimum detectable signal may be determined by either the noise level associated with the ion beam and the signal amplification electronics or by the background levels of a particular component on the instrument. Without definition of the particular instrument, it is not possible to determine which will be the controlling factor. However, concentrations of the order of one part per million are detectable for slow scan rates with some flight mass spectrometers.

The major background masses are usually 2, 18, 28 and 44; minor masses include 4, 12 and 40 and depend somewhat on the type of vacuum pump employed and the sample history in the instrument. The background at mass 28 might be considered in some detail since this will probably set a lower limit to the amount of nitrogen which can be detected in the Venus atmosphere and forms one criteria for the degree to which the carbon dioxide content of the sample should be reduced by the lithium hydroxide reaction.

Background levels, particularly at m/e 28, are dependent on the temperature at which the source is operated. Normally, a mass spectrometer will be outgassed at temperatures in the range of 250 to 300°C while pumping with a high speed vacuum system. Gases sorbed on the surfaces are pumped out and when the source is operated at temperatures of the order of 150°C, background levels improve significantly. However, if the source is operated at temperatures approaching those at which the system was outgassed, the background levels are higher. For typical flight mass spectrometers with source temperatures in the range from 150 to 200°C, the mass 28 background is of the order of 2×10^{-8} mbar. For maximum source operating pressure for a selected design value of inerts, the minimum detectable nitrogen mole fraction is given by:

$$X_{N_2}/\min = 2X_{i, \text{ design}} \frac{P_{\text{bkgd}/28}}{P_s / \max}$$

for a signal to background ratio of two.

$X_{N_2/min}$ = minimum detectable mole fraction of nitrogen in the atmosphere

$X_{i/design}$ = design value for mole fraction of inert

$P_{bkgd/28}$ = background pressure at mass 28

$P_{s/max}$ = source pressure for maximum flow

For

$$X_{i/design} = 0.02$$

$$P_{s/max} = 1.3 \times 10^{-4} \text{ mbar}$$

$$P_{bkgd/28} = 2 \times 10^{-8} \text{ mbar}$$

$$X_{N_2/min} = 6 \times 10^{-6}$$

The minimum detectable value will increase for higher source operating temperatures. If these minimum detectable levels for nitrogen are to be achieved, the carbon dioxide level has to be reduced to a correspondingly low value in the inlet system. The carbon monoxide fragment ion is about ten percent of the base peak at mass 44. If the mass spectrometer limiting values are to be approached, the carbon dioxide content must be reduced to levels on the order of 6×10^{-5} the original inlet system pressure.

Interferences with the noble gas determinations are summarized in Table 2. (It is assumed that organics are negligible in the system.)

The interferences of primary concern are those of CO_2^{++} with ^{22}Ne and the $^{40}Ar^{++}$ with $^{20}Ne^+$. Removal of carbon dioxide to very low concentrations will eliminate the interference with $^{22}Ne^+$. The interference between $^{40}Ar^{++}$ and $^{20}Ne^+$ can be eliminated by proper selection of electron ionization energy. Hydrogen chloride will also be eliminated by reactions with lithium hydroxide. Background levels for the inert gases are primarily a

TABLE 2.- Noble Gas Interferences

<u>Gas</u>	<u>Isotope/Abundance* (%)</u>		<u>Interfering Ions</u>
He	3	1.3×10^{-4}	C^{++}
	4	100	
Ne	20	90.92	Ar^{++} , HF^+
	21	0.257	
	22	8.82	CO_2^{++}
Ar	36	0.337	$H^{35}Cl^+$
	38	0.063	$H^{37}Cl^+$, HF^+
	40	99.60	$^{80}Kr^{++}$
	78	0.35	
	80	2.27	
	82	11.56	
	83	11.55	
	84	56.90	
	86	17.37	
	124	0.096	
Xe	126	0.090	
	128	1.92	
	129	26.44	
	130	4.08	
	131	21.18	
	132	26.89	
	131	10.44	
	136	8.87	

*Earth normal abundances

function of the sample history and the particular type of pump employed. The pumping speed of ion pumps for these gases is lower than that for nitrogen or carbon monoxide, so that background levels might be expected to be higher. Minimum detectable levels for these gases will thus be particularly dependent on sample history and the type of mass spectrometer system chosen for the large probe.

Carbon dioxide reaction rate.— The Venus atmospheric pressure at the start of the sampling period is 29 mbar and increases during descent. For a minimum volume system, the sampling pressure will be substantially higher than previously tested. Furthermore, the time available for processing the sample is shorter for higher pressure samples. For the typical descent shown in Figure 5, the mass scan rate changes at approximately 46 minutes into the descent. Assuming that the sample is to be scanned before this time, the maximum time available for sample processing is about 40 minutes. It is necessary to postulate a reaction rate equation to examine the effects of sample pressure on the time necessary to reduce the carbon dioxide content to some low value. For this analysis, a first order rate has been assumed.

$$V_i \frac{dp_{CO_2}}{dt} = k_r p_{CO_2}$$

where

p_{CO_2} = carbon dioxide pressure in the inlet system. $p_{CO_2} \text{ (at } t=0) \approx p_s$

k_r = reaction rate constant

(The reaction rate constant includes a factor for the surface area of the reactant, lithium hydroxide (or the hydrate). That is,

$$k_r = k'_r S_{LiOH}$$

Assuming that a large excess of lithium hydroxide is employed, k_r is constant.)

The final pressure of carbon dioxide is given by

$$\frac{p_{CO_2/f}}{p_{CO_2/i}} = \exp \left(\frac{-k_r t}{V_i} \right)$$

Values of $k_r t$ necessary to reduce the carbon dioxide content to some predetermined r level were calculated from this equation. A plot of these values is shown in Figure 7 (solid line) as a function of inlet system volumes for

$$\frac{P_{CO_2/f}}{P_{CO_2/i}} = 10^{-4}$$

Assuming that one half the available time (after the sample is taken) is allotted to the reaction of carbon dioxide with lithium hydroxide, the minimum value of k_r required can be calculated from these values. Figure 7 (dash line) shows these values for the typical descent curve.

The rate constant, k_r , can equally well be considered a conductance value for a valve connecting the lithium hydroxide cell to the sample volume. The calculated values indicate that for larger volume systems, higher reaction rates or larger conductances are required to achieve a fixed ratio of final to initial carbon dioxide content in the sample. All the calculated values of k_r are less than those measured in the Viking system (21 cm³/min).

These calculations indicate that it should be possible within limits to choose a small volume for the sample reservoir and process the sample within the time available during the descent. However, the assumptions should be considered carefully. The effect of temperature and pressure on the reaction rate cannot be reliably estimated, as was pointed out in the discussion of the chemistry of the reaction. The volume occupied by the inert gas chemical pump includes, in addition to the volume of the reservoir, the volume occupied by the cells or chambers containing the chemicals and the valves. For very small volumes for the reservoir, the major part of the system volume will be in the cells and valves. Beyond some value which must be defined for specific valves, changing the volume of the reservoir may not significantly impact the total system size.

Sorbent quantities.— At least three moles of lithium hydroxide are required to react with each mole of carbon dioxide to form the hydrate from the water evolved. One milligram of lithium hydroxide is equivalent to a sample of 880 mbar cm³. However, it is clearly desirable to employ a fairly large excess to promote rapid reaction with carbon dioxide and water. A 100-fold excess, approximately 100 mg, should be adequate to obtain rapid reaction.

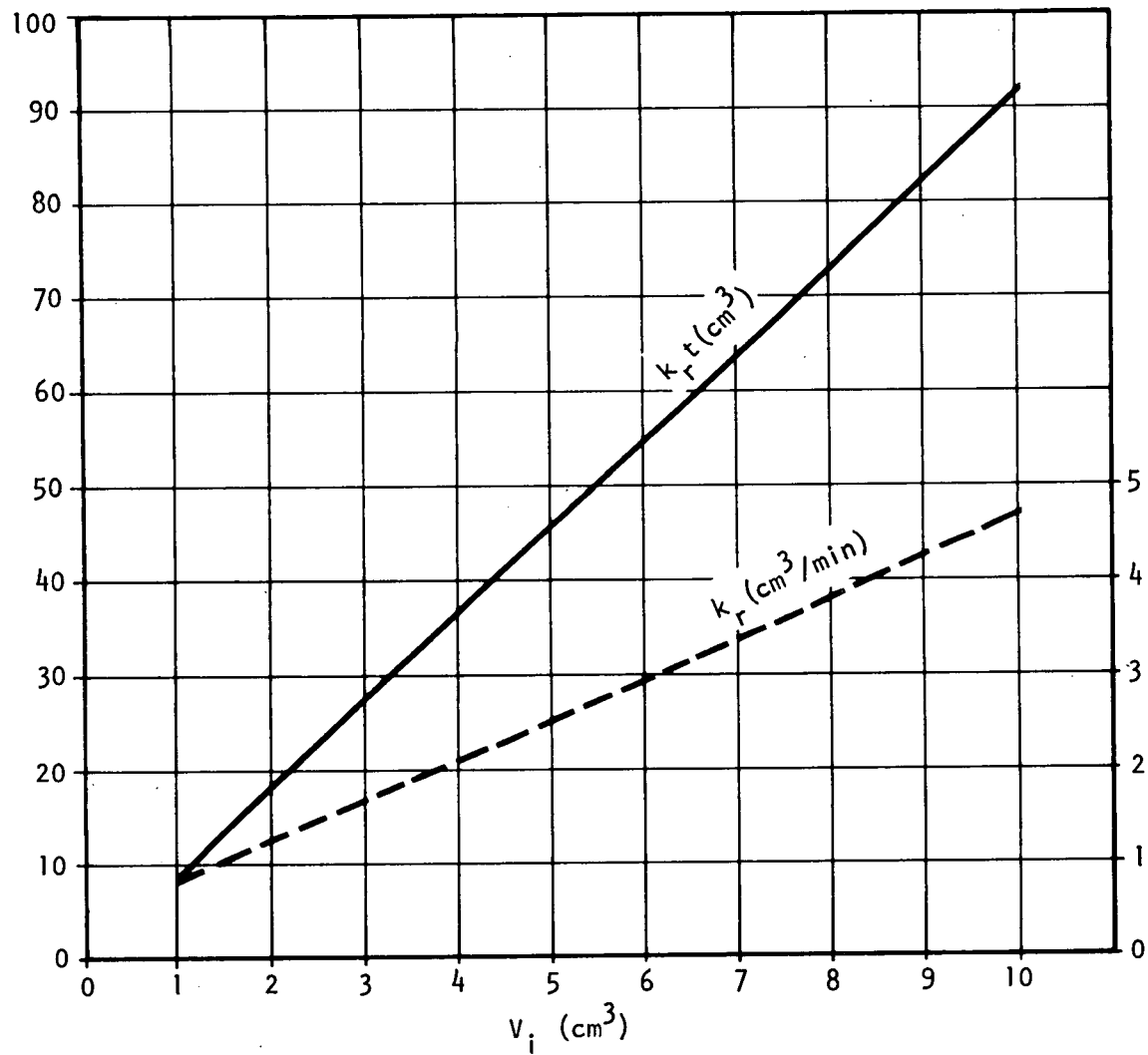


FIGURE 7.- Values of $k_r t$ for $p_f = p_i \times 10^{-4}$ and Minimum k_r
Values for Available Sampling Time

Potentially, the magnesium perchlorate desiccant would be required to absorb an amount of water equivalent to the amount of carbon dioxide in the sample. At a minimum, based on formation of the dihydrate, this would require 8 mg. In the tentative design, a 50-fold excess was chosen to provide adequate desiccant capacity.

The form of the lithium hydroxide must also be established. Fairly strong evidence exists that lithium hydroxide hydrate must be present to initiate the reaction, even though the Viking test data do not completely support this theory. The amount of hydrate present should be sufficient so that when the lithium hydroxide chamber is opened to the sample reservoir, all of the hydrate present will not decompose in attaining the equilibrium water vapor pressure. This is a function of the system volume.

$$\frac{V_i p_E}{RT} \times 42 = \text{minimum weight of hydrate (mg)}$$

where

V_i = volume of the inlet system

p_E = vapor pressure of the hydrate at T

T = temperature

R = gas constant

For gas solid reactions, the surface area of the solid, or the surface to volume ratio of the system, is usually a critical parameter. Both granular reagents and pressed pellets have been employed in tests of the carbon dioxide reaction; however, there is little documented distinction between the reaction rates. The materials used were made porous by dehydrating the hydrate or by vacuum sublimation of naphthalene from a pressed mixture of lithium hydroxide and naphthalene. There may be advantages to the latter technique since the pores created might be larger and more readily allow access of water vapor to the interior of the lithium hydroxide crystals. These parameters should be established in the test program for the chemical pump for the Venus probe mission.

Design considerations.— In the preceding sections, certain factors have been reviewed in relation to a system designed with four valves, a sample volume reservoir, and two chambers for chemical reagents. Some

consideration has been given to the possibility of eliminating the valves on the sample chambers. This does not appear feasible at the present time for the following reasons. If the valve on the lithium hydroxide chamber is eliminated, the entering gas will react with the lithium hydroxide, creating a pressure differential between the sample reservoir and the probe sample intake line. Sample flow could be controlled by a restrictor in the line between the reservoir and the probe sample line. Back diffusion of the inert gases and water could be minimized by choosing a capillary line flow restrictor. Such a system would require a longer time for sampling to obtain a fixed pressure of inerts since the flow would be restricted. Without the capability for isolating the lithium hydroxide, all of the water in the vapor phase, and that tied up in the form of the hydrate, would have to be pumped by the magnesium perchlorate. Both of these factors would lengthen the time required for sampling and processing the sample. The absence of a valve on this chamber would make it inconvenient to carry out preflight testing of the system. If the magnesium perchlorate cell is not valved, water formed by the reaction of carbon dioxide will be sorbed by magnesium perchlorate and if the reaction requires the hydrate, it would stop. The other two valves are necessary, one to terminate the sampling period and the other to prevent gas from the sample reservoir from entering the mass spectrometer while the atmospheric monitoring is in process.

A volume of 10 cm^3 was selected for the sample reservoir. This is a conservative choice since the sampling pressure of the order of 100 mbar can be employed with less than five percent change in flow rate for a system design based on two percent residuals. Smaller reservoir volumes can be implemented if the reaction with carbon dioxide is shown to proceed satisfactorily at the higher pressures. With this volume for the sample reservoir, the system volume exclusive of the valves is estimated at approximately 30 cm^3 . Assuming a comparable volume for the valves, reducing the sample reservoir volume to one cm^3 , for example, decreases the system volume by approximately 50 percent. It would require a 10-fold increase in pressure to achieve the same total amount of sample, with the attendant uncertainties of the carbon dioxide reaction at these high pressures.

Tentative values for the maximum leak rates through the valve seats is less than $10^{-7}\text{ cm}^3/\text{second}$ for valve one and valve four based on the effect on the nitrogen measurement and on potential interference with the analysis of direct atmospheric samples respectively. It is expected that somewhat higher leakage rates could be tolerated for the other valves, but these will depend on the sequence of preflight operations and test. The con-

ductance of the valves for the sample chambers should be in excess of $0.5 \text{ cm}^3/\text{sec}$. This limitation applies primarily to the diffusive conductance which will control the latter phases of the reaction.

Operation temperature for the system will depend on the ambient temperature in the probe. It has tentatively been assumed that this temperature will be less than 50°C . Operating data for the carbon dioxide reaction at temperatures in excess of this value are not currently available but it is deduced that the rates will be significantly affected if ambient temperatures are much in excess of 50°C .

The volume between valve four and the inlet leak should be minimal so that pumpout will occur rapidly when valve four is closed at the end of the inert gas measurement. A time constant of the order of 15 seconds might be appropriate. For the design parameters described above (10 cm^3 sample volume, two percent residuals, five percent change in flow rate in 180 seconds) the volume should be less than 40 microliters. This volume must be smaller for higher pressure samples.

One other feature of this system deserves some discussion. In designing the system to obtain maximum sensitivity for the inert gas measurement, the potential for overpressurizing the mass spectrometer is relatively high. If valve four should open before the carbon dioxide reaction has taken place, the source pressure could increase to values of the order of $6 \times 10^{-3} \text{ mbar}$, a factor of 40 above usual operating pressures. Some pressure override protection system should be included in a final system design to prevent this from happening.

Within the framework of the present experiment definition, it is difficult to devise a system design which is optimum from every standpoint. Factors which must be considered in the design have been presented and the effects of parameter variations on the overall experiment goals have been assessed. Limitations on the available experimental data for the lithium hydroxide reaction at high pressures of carbon dioxide have also been pointed out.

Chemical Pump for Ballast Volume Replacement

In preliminary planning for the Venus probe experiments, methods for obtaining a continuous, representative sample of the Venus atmosphere for mass spectrometric analysis were considered. In this system shown in Figure 2, a continuous flow of Venus atmosphere passes through an inlet reservoir as the probe descends through the atmosphere. Three flow

restrictors control the flow of gas entering the reservoir over different pressure ranges in the atmosphere. Flow out of the reservoir is maintained by a pump which pumps gas into an initially evacuated ballast volume. A chemical pump is proposed to replace the ballast volume. This chemical pump, reacting with the major component of the atmosphere, provides the driving force for moving gas through the system. The reaction of lithium hydroxide with carbon dioxide is also used in this application.

The chemical pump design involves consideration of the pumping speed required to maintain a pressure gradient for flow through the inlet system. To size the pump, the anticipated or required flow rates must be estimated. Pump speed is determined by the reaction rate constants reviewed in the chemistry section. The flow rates and pressure gradients are determined primarily by the inlet system design. Certain inert components in the Venus atmosphere will not react with a chemical pump based on the lithium hydroxide reaction. The pressure of these components in the chemical pump will increase continuously during the descent through the Venus atmosphere. In addition, the reaction of lithium hydroxide produces water which forms a hydrate with lithium hydroxide. The vapor pressure of this hydrate is present in the pump volume once the reaction starts. These components will diffuse back to the inlet system. Back diffusion can be minimized by using a relatively large volume for the chemical pump so that the pressure of inerts is low, or by making the diffusive conductance of the line between the sample volume and the chemical pump flow. Since volume is a constraint for the total probe system, the better approach is to minimize the diffusive conductance. Therefore, for this application, the pump design was premised on the use of a long capillary line to connect the chemical pump to the inlet system at the point at which the gas sample enters the mass spectrometer.

During descent, there will be three pressure or flow rate cycles. The pressure at the mass spectrometer can be allowed to vary as the atmospheric pressure varies during each of the three cycles. But since the mass spectrometer leak rate must be chosen on the basis of the highest anticipated pressure, the full dynamic range of the mass spectrometer would only be available at the high pressure end of each cycle. If the pressure at the leak is held constant by varying the conductance of the line to the pump, the full dynamic range of the mass spectrometer would be continuously available. A system was therefore considered in which the capillary line is in series with a variable valve. It is assumed that pressure at the leak is held constant by varying the opening of the valve. At the high pressure end of each cycle, the valve is completely open and does not restrict the flow. The total pressure drop is taken across the capillary line. At the low pressure, low flow end of each cycle, the valve controls the flow with

the entire pressure drop occurring between the mass spectrometer inlet leak and the chemical pump.

The design and operation of the inlet system itself is not a part of this study program, but it was necessary to make some assumptions about possible operating conditions to design the system and to evaluate the amount of back diffusion of inert gases from the chemical pump.

Sample volume - pump speed.- The total sample to be processed during descent through the Venus atmosphere is postulated to be 0.3 bar liter,³ a relatively large volume of gas. Considering the descent time is typically 70 minutes and the maximum flow rate through the mass spectrometer is about 6.7×10^{-3} mbar cm^3 per second, the total sample required for the mass spectrometer is

$$\text{Total MS Sample} = 70 \times 60 \times 6.7 \times 10^{-3} = 28.2 \text{ mbar cm}^3.$$

A ratio of 100:1 would indicate a value of 3×10^{-3} bar liters for the total gas sample. This ratio is frequently used in bypass pumping sampling systems. The system design described in the following paragraphs is premised on a total sample volume of 0.3 bar liter, or a factor of 10^4 for sample bypassed to sample to the mass spectrometer. If the lower ratio can be accepted, the system design can be scaled down by at least a factor of 10.

A pressure differential is necessary to maintain flow between the mass spectrometer inlet leak and the chemical pump. For steady state flow at some rate into the inlet system, the reaction rate in the pump must be fast enough to maintain the pressure differential. This condition is given by

$$Q = R p_{\text{CO}_2}$$

where

Q = steady state flow rate into the pump

R = reaction rate

p_{CO_2} = pressure of carbon dioxide in the pump

(This equation is based on the assumption that the residual partial pressures are low). The value required for the reaction rate constant

is dependent on Q , the rate of flow into the system and the value of p required to maintain the pressure differential. For atmospheric leaks of fixed geometry as shown in Figure 2, the flow rate Q will change as the probe descends through the atmosphere. As a starting point in evaluating the value required for R , an average flow rate into the pump can be calculated, assuming that the flow rate is maintained constant while the probe descends in the atmosphere. This average Q_{AVE} is

$$Q_{AVE} = \frac{\text{Total Sample}}{\text{Descent Time}} = \frac{0.3 \text{ bar liter}}{70 \text{ min}}$$

$$= 71.5 \text{ mbar cm}^3/\text{s}$$

The value for R , the reaction rate constant, can be derived from the Viking data. Experience with the Viking Mass Atmospheric Filter System indicates a value for R of $0.28 \text{ cm}^3/\text{s}$ for a 100 mg charge of lithium hydroxide, with the limitation that this value may be more a function of the valve conductance. The highest value reported in a laboratory system is $4 \text{ cm}^3/\text{s}$, also for a 100 mg of lithium hydroxide. From these values, the pump pressure for the average flow rate would be 255 mbar for $R = 0.28 \text{ cm}^3/\text{s}$, and 17.9 mbar for $R = 4 \text{ cm}^3/\text{s}$. From these calculations, satisfactory operation of the pump would be obtained if the faster reaction rate were realized.

In general, the rate of gas solid reactions can be increased by increasing the surface-to-volume ratio for the system. A complete rate expression for such a reaction is

$$V \frac{dp}{dt} = k p A$$

where

- V = system volume
- p = gas pressure
- t = time
- k = reaction rate constant
- A = activity of the solid phase

From this expression, for a system with a fixed volume and amount of sorbent, the reaction rate constant can be redefined

$$k^1 = \frac{kA}{V}$$

where A, the activity of the solid phase, is related to the amount of sorbent in the system. There is no evidence that the reaction rates measured are limited by the surface area. It is theoretically possible to increase the reaction rate by increasing the amount of sorbent in the system for a fixed volume, but this would have to be verified experimentally. Furthermore, for systems where carbon dioxide is the bulk gas, it must be established more firmly that the reaction is occurring with the hydrate. The available data is somewhat ambiguous on this point.

Before choosing the amount of lithium hydroxide in the pump, it is advantageous to examine the volume requirements. In the originally proposed three liter volume system, a final pressure of 100 mbar would be present in the volume at the end of the descent.³ The pump was defined to have the capability of maintaining the flow rate against this back pressure. A similar pressure would presumably be acceptable for the chemical pump; but in this case, assuming fast reaction rates, the pressure would be mainly that due to the unpumped gases and water vapor pressures. Estimating the residual gas content at three percent, and the equilibrium vapor pressure of the hydrate

$$V \geq \frac{0.03 \times 3 \times 10^5 \text{ mbar cm}^3}{100 \text{ mbar} - 5.3 \text{ mbar}}$$

$$\approx 100 \text{ cm}^3$$

The stoichiometric amount of lithium hydroxide required for 0.3 bar liter of carbon dioxide is of the order of one gram, allowing one mole for formation of the hydrate. The volume occupied by one gram for granular material with a packing density of 0.42 g/cm³ (estimated from data in Reference 4) is 2.4 cm³ and the free gas volume associated with one gram is estimated at 1.6 cm³, for the crystalline density of 1.5 g/cm³. Part of the free gas volume is associated with pores in the sorbent and part with the external volume. If it is estimated that roughly half of the calculated free gas volume is in the pores and not readily accessible, about 0.8 cm³ of volume is available for one gram of sorbent in the pump. To obtain the required free gas volume for a pump packed with lithium hydroxide would require 125 grams of lithium hydroxide and the pump would have a volume of approximately 300 cm³. A tentative design was selected using 60 grams of lithium hydroxide and allowing 50 cm³ of unpacked volume for circulation of the gas to the surface of the lithium hydroxide. The

total pump volume for this system is 200 cm^3 . This somewhat arbitrary choice gives a fairly high ratio of weight to volume (0.6 g/cm^3) for the pump system and allows some flexibility in designing the lithium hydroxide containment system. Part of the lithium hydroxide should be in the form of the hydrate. The crystalline density of the hydrate is nearly equal to that of the anhydrous material; the bulk density is not known.

System size is premised on a total sample volume of 0.3 bar liter. Arguments for a smaller sample volume were presented in the introductory section. If the 100:1 bypass pumping ratio could be accepted, the system volume and weight could be reduced by at least a factor of 10.

Flow rate range.— The flow rate range for the system with three fixed leaks, shown schematically in Figure 2, may be derived from the postulated total sample of 0.3 bar liter. If the pressure range from 29 to 94000 mbar is divided geometrically into three segments, the ratio of the maximum to minimum pressure is 14.8.

$$\text{Pressure Range} = \left(\frac{94,000}{29} \right)^{1/3} = 14.8$$

The flow rate variation will depend on the mode of flow chosen for sampling the atmosphere. If a viscous leak is chosen, the flow rate range will vary as the square of the pressure range

$$Q_{\text{max}} = (14.8)^2 Q_{\text{min}}$$

(neglecting viscosity changes and pump pressure with respect to atmospheric pressure). For molecular flow

$$Q_{\text{max}} = 14.8 Q_{\text{min}}$$

Numerical integration of the flow equations for the descent time pressure profile shown in Figure 5 gives the flow rate range for the system. The flow rate will vary from 12.2 to 174 mbar cm^3/s for molecular flow and from 1.5 to 322 mbar cm^3 for viscous flow for a total sample volume of 0.3 bar liter.

$$\text{Total Volume} = 3 L_M \int_{29}^{14.8 \times 29} p dt \quad \text{for molecular flow}$$

$$\text{Total Volume} = 3 L_V \int_{29}^{14.8 \times 29} p^2 dt \quad \text{for viscous flow}$$

The viscous flow mode is utilized in the design calculations primarily because it is difficult, if not impossible, to obtain leaks which are molecular at pressures much in excess of several bars.

At the high flow rate end of the range a pumping speed or reaction rate for carbon dioxide of the order of $16 \text{ cm}^3/\text{s}$ would be required to maintain a pump pressure of carbon dioxide of the order of 20 mbar.

$$k = \frac{Q_{\max}}{p_{\max}} = \frac{322}{20}$$

This is a higher rate than has currently been demonstrated for the lithium hydroxide reaction in the static systems. Nevertheless, it is not unreasonable to expect that such rates may be achieved in the larger reactor system proposed for the chemical pump.

Back diffusion from the chemical pump.- To estimate back diffusion rates from the chemical pump, it is necessary to make some assumptions about the mechanism of flow and the inlet system pressure. The pump system is designed with a capillary flow line connecting it to the inlet system. Gas flow was assumed to be viscous through this line with a mass flow rate varying from $1.5 \text{ mbar cm}^3/\text{s}$ to $322 \text{ mbar cm}^3/\text{s}$ during each of three cycles.

Two approaches to the inlet system operation were considered. In one, it was assumed that the pressure at the mass spectrometer leak was allowed to vary with the intake atmospheric pressure. At the start of each leak cycle, the pressure would be low and would increase to the end of the cycle. Each successive cycle would start at a higher mean pressure in the line and the intake leaks would be sized to accommodate this condition. In the

other, the pressure at the mass spectrometer intake leak was maintained constant at some relatively high value. In this case, the system would contain a variable flow rate valve between the mass spectrometer inlet leak and the capillary line to the pump. At the start of the cycle, when the flow rate is low, the valve would be the flow controlling device and the pressure drop between the pump and the mass spectrometer leak would be entirely across the valve. As the pressure at the atmospheric leak increased, the pressure at the mass spectrometer leak would be held constant by opening the valve. The pressure drop would be distributed between the valve and the line, as two flow restrictors in series. At the maximum atmospheric pressure or flow rate through the system, the valve would be wide open and the entire pressure drop taken across the capillary line.

The model with varying pressure at the mass spectrometer leak is considered first. Viscous flow through the line requires that the diameter of the line be greater than 100 times the mean free path of the gas. This restriction is imposed at the low pressure outlet for the line, where the minimum pressure is expected to be 5.3 mbar at the start of the pump operation. The mean free path is estimated to be 8×10^{-4} cm and the required diameter of the line is 0.080 cm, or 0.040 cm radius. From the Poiseuille equation, the line length for a given pressure differential can be calculated.

$$Q = \frac{\pi r^4}{16 \eta \ell} (P_L^2 - P_p^2)$$

In this equation

- Q = flow rate
- r = radius of the line
- η = viscosity
- ℓ = length of line
- P_L = pressure of the leak
- P_p = pressure in the pump

For $\ell = 100$ cm, and $Q = Q_{\max} = 322 \text{ mbar cm}^3/\text{s}$

$$P_L = 100 \text{ mbar}$$

For $Q = Q_{\min} = 1.5 \text{ mbar cm}^3/\text{s}$

$$p_L = 8.8 \text{ mbar}$$

An estimate of the amount of back diffusion is derived by considering the case for steady state flow at the low end of the flow rate range. The flow rate due to back diffusion of component, i, from the pump is

$$q_i = \frac{\pi r^2 D}{\ell} \left(p_{i,p} - p_{i,L} \right)$$

where

q_i = flow due to diffusion (mbar cm³/s)

r = radius of the line

D = diffusion constant at the pressure in the line

ℓ = length of the line

$p_{i,p}$ = pressure of component i at the pump

$p_{i,L}$ = pressure of component i at the leak, due to back diffusion

The rate at which component i is transported down the line due to viscous flow is

$$q_i = \frac{Q p_{i,L}}{p_{t,L}}$$

where

$p_{t,L}$ = total pressure at the leak

In steady state the pressure of component i at the leak is determined by equating the flow rates

$$\frac{Q p_{i,L}}{p_{t,L}} = \frac{D \pi r^2}{\ell} \left(p_{i,p} - p_{i,L} \right)$$

The applicable value of the diffusion coefficient is given by:

$$D = \frac{D_r p_r}{p}$$

where

D_r = diffusion coefficient at 1000 mbar and 25°C

p_r = 1000 mbar

p = local pressure

$$p_{i,L} = \frac{p_{i,p}}{1 + \frac{Q_l}{1000 D_r \pi r^2}}$$

For water

Q = 1.5 mbar cm³/s

$p_{i,p}$ = 5.3 mbar for water

D_r = 0.150 cm²/s

$p_{i,L}$ = 0.027 mbar

The total pressure at the leak is 8.8 mbar; the water content due to back diffusion is of the order of 0.3% and only relatively high concentration of water would be detectable. At higher operating temperatures, the partial pressure of water in the pump will be higher and back diffusion to the inlet system will be higher. At 50°C, for example, the equilibrium vapor pressure is of the order of 20 millibars. This will increase the estimated pressure at the inlet system by a factor of four.

At the end of the cycle, when the flow rate is 322 mbar cm³/s, the pressure due to back diffusion of water is 2×10^{-4} mbar. Water in the incoming sample could readily be detected at low concentration levels.

Back diffusion of inerts assuming a pump pressure of 30 mbar inerts at the end of the first cycle would increase the pressure at the leak by 8×10^{-4} mbar. At the start of the next cycle, with flow into the system of $1.5 \text{ mbar cm}^3/\text{s}$, the pressure of residuals due to diffusion from the pump is estimated to be 0.145 mbar from the approximation. The total pressure at the leak at that time would be of the order of 38 mbar. The error due to back diffusion in this case is approximately 13 percent, if the steady state were reached, and assuming that the residuals represented three percent of the gas stream. When one leak is closed in the system and the flow rate into the inlet system drops, there will obviously be a short time interval during which the rate of back diffusion is high. However, it is doubtful that the steady state level would be reached nearly instantaneously.

Similar results are obtained for the second model described with the variable flow control valve. In this case the transport line was designed to be 240 cm long and the constant pressure at the intake leak to the mass spectrometer was of the order of 150 mbar. The valve dimensions were approximated by assuming that the conductance in viscous flow was that of one centimeter long tube, and calculating an equivalent diameter.

$$\begin{aligned} \frac{r^4}{\ell} &= \frac{16 \eta \ell Q}{\pi \left(p_\ell^2 - p_p^2 \right)} \\ &= \frac{16 \times 145 \times 10^{-6} \times 1.5 \times 10^{-3}}{\pi \times 10^3 (150^2 - p_p^2)} \\ r &= 2.6 \times 10^{-3} \text{ cm for } \ell = 1 \text{ cm} \end{aligned}$$

From this

$$\begin{aligned} p_{i,\ell} &= \frac{p_{i,p}}{1 + \frac{Q\ell}{1000 D_r \pi r^2}} \\ &= \frac{5.3}{1 + \frac{1.5 \times 1}{1000 \times 0.150 \times \pi (2.6 \times 10^{-3})^2}} \\ &= 0.01 \text{ mbar} \end{aligned}$$

At the start of the analysis, the flow control valve would be closed until the atmospheric pressure exceeded 150 mbar. At that point, the valve would open and gas would flow down the line. Back diffusion of water, assuming the full pressure drop across a valve, is estimated at 0.01 mbar, from the steady state approximation, assuming a diffusive resistance for a flight type valve appropriate to the flow requirements postulated. This case represents a worst case for water for this system. With this model, calculations for other residuals are also very small.

These calculations are only used to formulate some approximations of diffusion effects which may occur in an actual system for certain flow rate and pressure conditions. Better calculations for back diffusions would be carried out if the interface between the inlet system and the pump were defined, and a better model of operating conditions established.

Summary

The pump design was formulated with the long capillary line connecting it to the inlet system. This approach should minimize diffusion problems. The actual line required must be determined from the inlet system operating conditions. If the constant pressure, variable flow approach is adopted, a suitable flow regulating valve must be identified. The original concept implied that the chemical pump was a replacement for the ballast volume and would interface with the inlet system through the mechanical pump. It appears feasible, based on the considerations described above, to employ a direct interface to the chemical pump, eliminating the mechanical pump entirely. This approach is equivalent to a capillary sampling line with a variable intake pressure, and appears to have considerable merit, particularly if a smaller total sample volume could be used.

MECHANICAL DESIGN

Preliminary designs for the two chemical pumps are based on the design analysis presented in the preceding section. The mechanical design objectives are maximizing exposure of the gas to the sorbent and preventing migration of the sorbent through the system. A double containment approach has been used to achieve these objectives. In both systems, the sorbent is retained by a supported screen tubular element.

Retention of lithium hydroxide has presented difficulties in the past¹⁰ and it is anticipated that some experimental effort will be involved in establishing optimum access to the lithium hydroxide while minimizing the migration of the chemical through the chamber to the valve seat. In line with these considerations, a design philosophy was adopted in which sensitive areas, such as valve seats or small dimensioned lines, would be protected by a fine (5 to 20 micron) screen, placed over a large area to prevent reduction in conductance, while primary containment of the chemical is achieved by a relatively coarser screen material. The chemicals will be sieved to obtain a known particle size range for the cells. The retaining screen will have smaller openings. As an alternative, porous pressed pellets sized to fit within the tubular assembly will be considered.

A limited design effort was undertaken to arrive at a tentative configuration for the pumps. It is recognized that a final system design depends on location of the pump within the probe and the interfaces of the pump with the mass spectrometer and the sample intake line. It also depends on the valves chosen for the system. Selection of valves was not included in this study effort.

Inert Gas Chemical Pump

The inert gas chemical pump consists of a sample gas reservoir and two valved chemical sorbent cells. A valved sample intake line connects the gas reservoir with the large probe sample inlet line. The reservoir interfaces with the mass spectrometer through a sintered metal flow restriction which is also valved. Isometric and detailed drawings of the inert gas pump are shown in Figures 8 and 9. A sample of gas enters the reservoir through the valved intake line and the valve is closed to terminate the sampling interval. The sample is exposed sequentially to lithium hydroxide and magnesium perchlorate contained in individual sorbent cells. After processing, the cells are valved off from the reservoir and the residual gases are admitted to the mass spectrometer by opening the valve to the sintered metal leak.

The sample volume reservoir and sorbent chemical cells are machined from a single block of stainless steel. Slant holes are drilled into the block to interface the reservoir with the valves controlling access to the chemical reactant cells. The valves are mounted to the block with retaining clamps. The sorbent cell tops and reservoir closure plate are electron beam welded to the main module body and the mass spectrometer leak assembly is mounted on the reservoir closure plate.

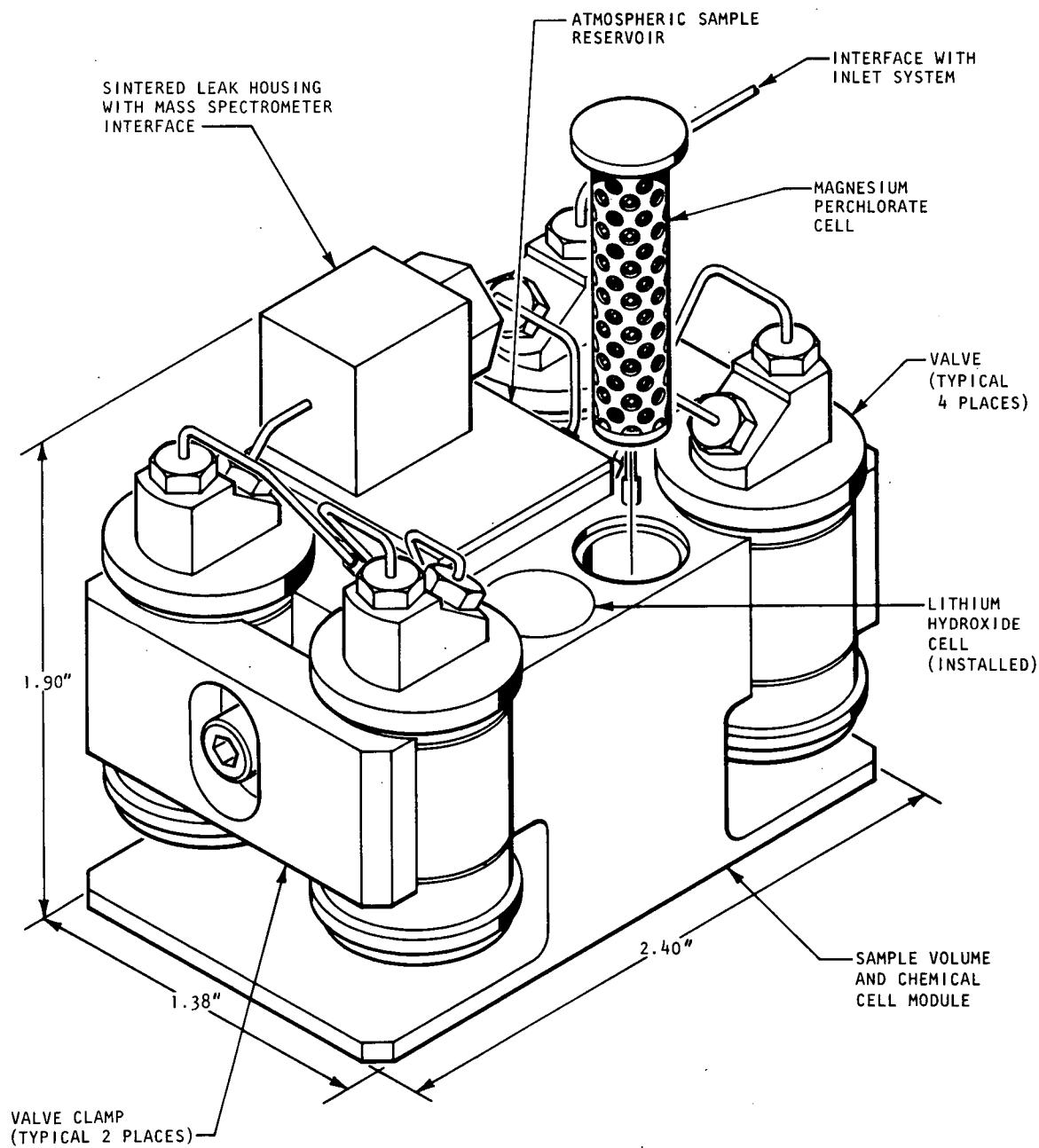


FIGURE 8.- Chemical Pump for Inert Gas Measurement

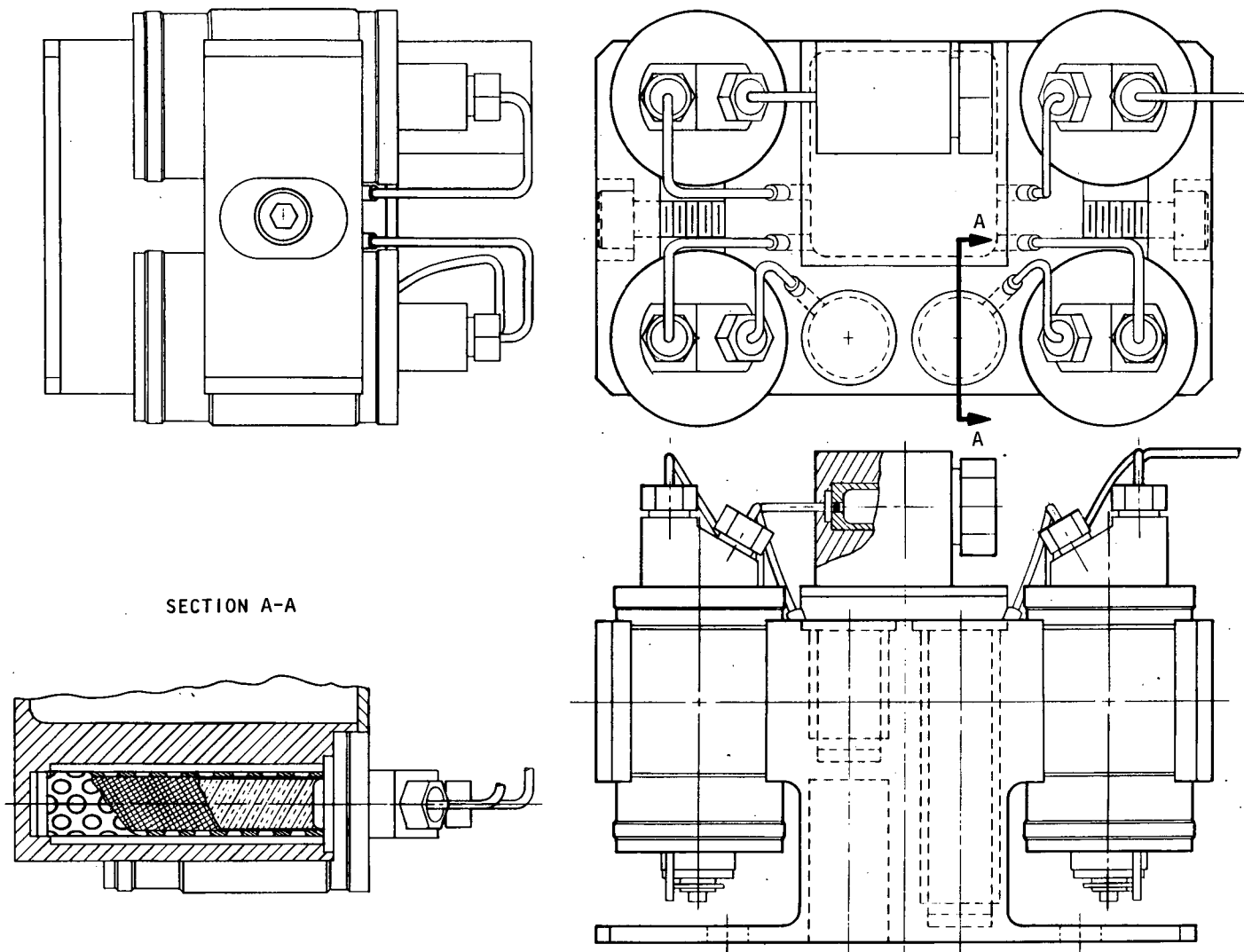


FIGURE 9.- Details of the Inert Gas Pump

Tubular assemblies, positioned on the axis of the cylindrical sorbent cell chamber, contain the chemical charges. The tubular assembly consists of a reinforced mesh screen, attached to the inside circumference of a perforated stainless steel tube, and end caps which retain the chemicals within the tube. The tubular assembly is located in the center of the chamber by means of a recessed locating hole. A port drilled in the outer wall of the chamber connects the chamber to the valve. This port has a hemispherical opening at the sample chamber wall, covered by a fine mesh screen as a secondary barrier to prevent migration of chemicals to the valve seat. The chemical cartridges are designed for maximum exposure of the sample gas to the reactants and to prevent migration of fine particles through the system. Screen mesh sizes have not been chosen at the present time, but should be established in the evaluation program. The system is fabricated from 316 series stainless steel and the retaining screens are made from nickel.

The four valves in the system should be capable of repeated operation for the test program. For a final system, the valve to the probe intake line and the magnesium perchlorate cell could be replaced by a single shot valve. The valves on the lithium hydroxide cell and the mass spectrometer intake leak, would require two single shot valves for opening and closing these elements. If the rate of the reaction is not to be restricted, the valves must have relatively high conductance. Allowable leak rates for the sample intake valve and the mass spectrometer leak valve should be less than 1×10^{-7} cm³/s. Higher leak rates of the order of 1×10^{-5} cm³/s can be tolerated for the chamber valves. The leak rate for the intake valve was determined on the basis of carbon dioxide leakage after the sampling period is terminated. The maximum leak rate for the mass spectrometer intake valve is determined from the effect of leakage on the ion source pressure. To protect the mass spectrometer in the event of system failure, a pressure sensor on the gas sample reservoir was considered. The necessity for including such a device is dependent on the particular mass spectrometer and valves chosen, and may be better established at system level analysis.

A volume summary is presented in Table 3. To some extent, the volume of the system depends on the particular valves to be utilized and on the interface to the mass spectrometer. The system design shown in Figures 8 and 9 represents an approach to a relatively compact unit; however, configuration can be changed to meet the requirements for a particular placement within the system.

TABLE 3. - Volume Summary

Sample Reservoir	11 cm ³
Lithium hydroxide chamber	1.3 cm ³
Magnesium perchlorate chamber	2.5 cm ³
Module containing the sample reservoir and chemical chambers	30 cm ³
Leak assembly	2.2 cm ³
Base plate	2.7 cm ³
Valve mounting hardware	1.4 cm ³

Chemical Pump For Ballast Volume Replacement

The basic components of this system are a lithium hydroxide sorbent chamber and associated free gas volume contained within a cylindrical assembly, and a valve and capillary connecting the chamber to the inlet system interface. The valve is used to isolate the pump from the capillary and inlet system for preflight test and to prevent migration of water vapor from the sorbent during storage. The unit is shown in Figures 10 and 11.

The sorbent is retained within a cylindrical annulus created by an internal cylindrical screen assembly and the outer wall of the pump chamber. The internal screen assembly consists of a perforated stainless steel tube with a reinforced screen spot welded to the outer surface. This cylindrical assembly is held in place by shoulders machined in the base mounting plate and in the sorbent retaining assembly. The sorbent retaining assembly is a sandwiched structure, a fine reinforced screen retained between two plates. The lower plate has a machined shoulder for positioning the inner cylindrical element. The upper and lower plates have a hole pattern drilled in the center section which interfaces with the center cylindrical gas space to afford a double barrier between the gas entrance and the sorbent. The whole assembly is electron beam welded to the outer wall of the pump. The top closure plate has a ribbed structure which presses on the sandwiched assembly retaining it in place. The capillary tube is attached to the top closure plate.

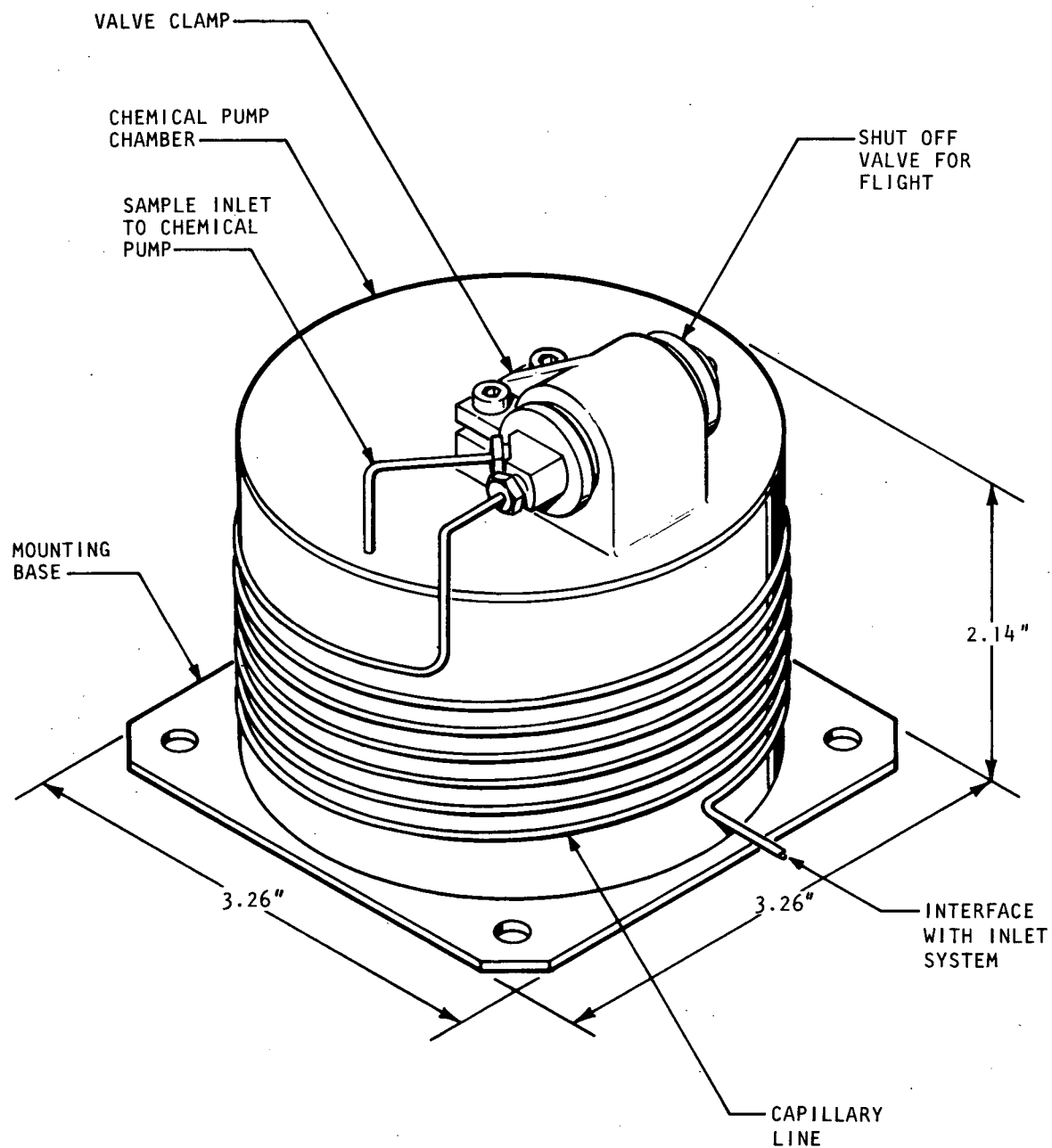
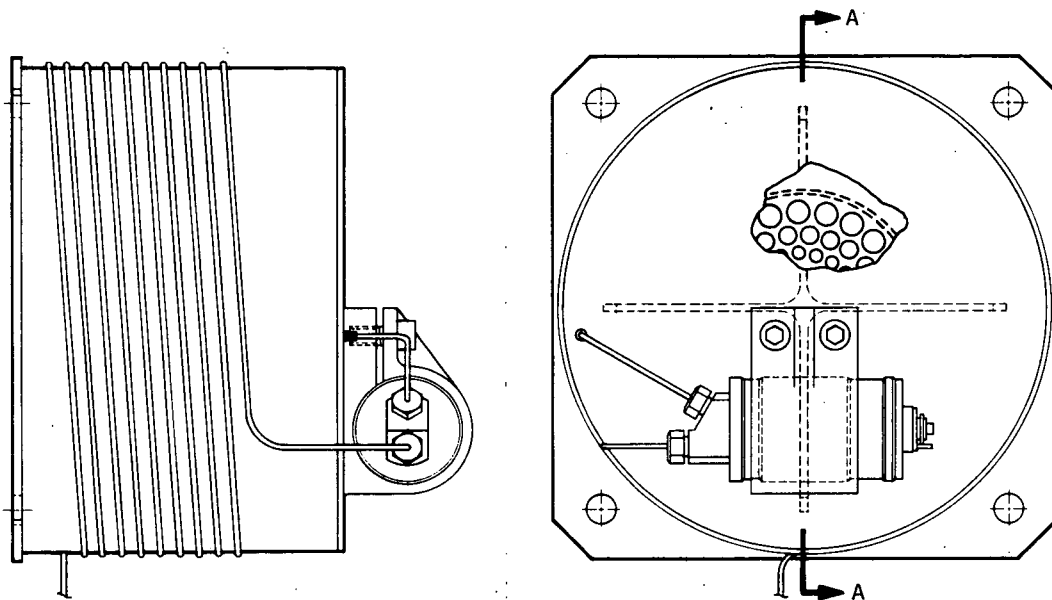


FIGURE 10.- Chemical Pump for Ballast Volume Replacement (Dynamic System)



SECTION A-A

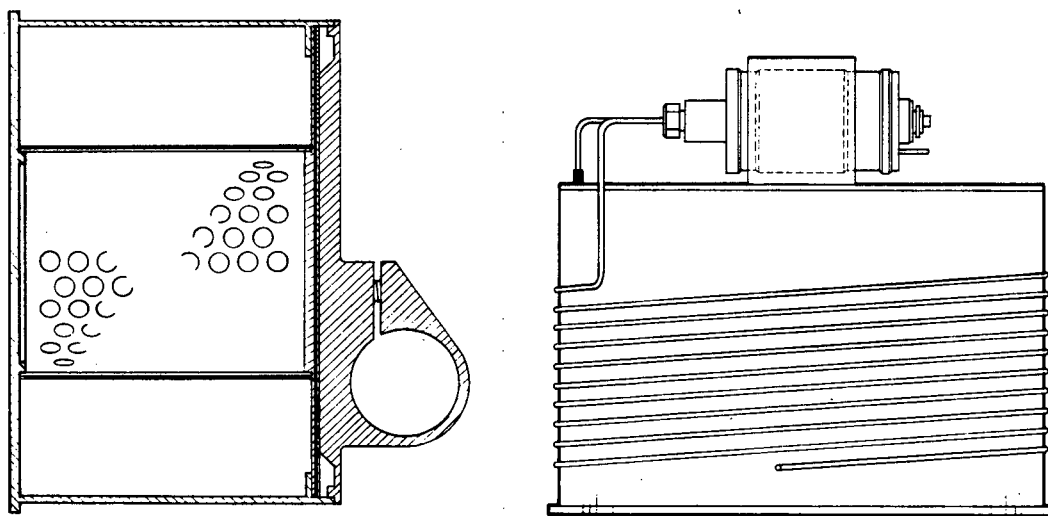


FIGURE 11.- Details of the Ballast Volume System

For the engineering evaluation model, the top closure would be effected by a clamp-flange and O-ring assembly. Provision for evacuating the pump chamber and connecting it to vacuum/gas manifold for test will be made through the base mounting plate.

The gas enters the cylinder through a capillary attached to the top plate of the assembly at an off-axis location, in the gas space between the sandwiched screen assembly and the chamber top plate. The capillary is wrapped around and attached to the outside of the pump chamber for structural integrity and positive location. The inside diameter of the capillary is 0.080 cm; the effective length is approximately 250 cm.

Approximately 60 grams of pelletized lithium hydroxide is contained in the pump for reaction with carbon dioxide. The total module weight, exclusive of the valve, is approximately 200 grams; the volume is 240 cm³.

FABRICATION AND TEST PLAN

Inert Gas Pump

A test system will be fabricated to simulate the preliminary system design previously described. The system will be identical to the proposed Venus system except that, to facilitate testing, closure of the chemical chambers will be made by clamp flange and metal O-ring seals to facilitate replacement of the solid chemicals between experiments. Valves were selected as typical of flight hardware for purposes of estimating the system size. It is assumed that valves for a test system would be supplied by NASA Ames on the basis of the results obtained from their evaluation program. As an alternate approach, the test system could be equipped with all metal laboratory vacuum valves, resulting in a considerable savings in cost. The difference in conductance between the flight valves and the laboratory valves could be estimated and a reasonably close approximation for test purposes made by short tube sections. The effect of increased dead volume is expected to be minimal. If laboratory valves are used, the engineering evaluation model would be reconfigured to separate the sample reservoir from the chemical chambers for ease in assembly of the system for test purposes. This approach would allow individual parts of the system to be redesigned as required.

Parts for the system for laboratory test will be fabricated from engineering preliminary release drawings and assembled in the laboratory. Chemicals will be loaded into the cells in a dry atmosphere. The assembled

pump will be attached to a laboratory inlet system equipped with a sample reservoir and a pressure gauge. A laboratory vacuum system will be used to evacuate the inert gas pump and condition the cells to convert part of the lithium hydroxide to the hydrate for the test program. All systems will be checked for leaks prior to start of the test program.

Test plan engineering evaluation model.- The following plan is recommended for evaluation of the engineering model.

1. Reaction rate measurements.
 - a. Determine the reaction rate for carbon dioxide at three initial pressures in the range from 20 to 400 mbar for anhydrous, granular lithium hydroxide and for a mixture of lithium hydroxide and lithium hydroxide hydrate. Measure sorption rate of $\text{Mg}(\text{ClO}_4)_2$ for water in sample volume from the lithium hydroxide reaction.
 - b. Repeat the reaction rate measurements for carbon dioxide and water at three temperatures in the range from 25°C to maximum anticipated ambient aeroshell temperature.
 - c. Investigate the advantage of using a pellet of lithium hydroxide in place of granular material for containment and compare reaction rates.
 - d. On the basis of the above measurements and defined operational goals and parameters, review the design and incorporate design changes as required. Repeat measurements to verify performance of redesigned system. A principal anticipated change is the screen mesh size used for containment of lithium hydroxide.

The reaction rate measurements are to be accomplished by following the decay of the carbon dioxide pressure in the sample reservoir with time. The initial test in each series will be made with anhydrous lithium hydroxide. Rates for the hydrate will be made with successive charges of carbon dioxide. Repeated measurements will be made with anhydrous lithium hydroxide, if it appears that the reaction proceeds rapidly.

2. Residual gas measurements.

With the operating conditions (time, pressure, temperature, lithium hydroxide and hydrate and system design) resulting from the reaction rate measurements, determine inlet volume residuals

for test gas containing nitrogen, argon, and carbon monoxide at three selected low concentrations less than five percent in carbon dioxide. For these measurements, the inlet system should interface with a mass spectrometer of known operating characteristics (source sensitivity, flow rate) through an inlet leak having a conductance approximating that to be used in the flight system. Background levels for the gases of interest should be established for the mass spectrometer and the inlet system prior to the residual gas measurements and concentrations of residuals to be tested. From these measurements, the minimum detectable levels for the inert gases in the Venus atmosphere, will be established.

Chemical Pump for Ballast Volume Replacement (Dynamic System)

The plan for fabricating this pump is based on a phased effort in which some preliminary laboratory experiments are to be performed to establish pump speed - pump pressure relationships for different ratios of sorbent weight-to-gas space volume in the pump. Performance requirements for the pump, total sample volume and maximum flow rate or pump speed, should be reviewed and modifications made to the existing design as indicated from the experiments. Pump size is determined to a large extent by the concentration of unreactive gases in the atmosphere. If more recent data indicates that the inert gas content might be less than the design value (three percent) the volume of the pump could accordingly be made smaller. The pump design would be fabricated and experiments conducted to verify pump speed - pressure relationships and to evaluate back diffusion to the inlet system under the defined inlet system flow rates and operating conditions.

The pump to be fabricated for these tests should include a port for connection of the pump to a vacuum manifold, with a pressure sensor and a water vapor reservoir for conditioning the sorbent. This pump, fabricated to engineering preliminary release drawings, utilizes clamp flange closures at the top closure plate to facilitate changing sorbent charges and screen mesh sizes as required. The system is assembled and leak checked prior to the start of tests. The test program, including preliminary experiments, is described in the following paragraphs.

The following test plan is proposed for the development of a chemical pump for replacement of the ballast volume in the Pioneer Venus large probe mass spectrometer.

1. Determine pump speed - pressure relationships for the lithium hydroxide (hydrate) - carbon dioxide pump at speeds up to 400 mbar cm^3/sec at ambient ($\sim 25^\circ\text{C}$) temperatures.

Establish the effect of pump gas space volume to sorbent weight ratio on the speed of the pump.

Determine the optimum ratio of anhydrous lithium hydroxide to hydrate for the proposed pump.

Determine pump speeds at three temperatures in the range from 25°C to maximum anticipated probe ambient temperature (TBD).

2. Review the pump design proposed in the Mechanical Design section and make design changes as required by the results of the tests described above, and the defined inlet system operation conditions.
3. Fabricate an engineering evaluation model pump for laboratory test.
4. Perform the following tests on the engineering evaluation model.
 - a. Measure pump speed as a function of pump pressure for speeds up to 400 cm^3/sec at temperatures near 25°C . Compare pump speeds and pressures with values established in the preliminary experiments (Item one) to verify the pump design and evaluate the effect of screens on pump speeds.
 - b. Determine pump speed - pressure relationship at the probe ambient temperature (TBD).
 - c. Determine diffusion rates of water from the pump to the inlet system at the probe ambient temperature and at three inlet system flow rates in the range from 1 to 400 mbar cm^3/sec .
 - d. Determine diffusion rates of inert gases from the pump for three levels of inert gas pressure in the pump in the range from 10 to 100 mbar and at three inlet system flow rates in the range from 1 to 400 mbar cm^3/sec .

APPENDIX

MASS SPECTROMETER
SENSITIVITY - FLOW RATE RELATIONSHIP

Sample flow rates through flight mass spectrometers are usually limited by power constraints for system operation. Within this constraint, various tradeoffs may be exercised to achieve the goals of a particular experiment. The source design may be optimized for sensitivity within limits for different values of sample flow rate. Table A-1 shows design parameters for three typical flight designs. In these instruments, the same ion current (I_{\max}^+) is obtained for three different flow rates.

TABLE A-1.- Mass Spectrometer Source Parameters

	<u>Symbol</u>	<u>Units</u>	<u>Low Flow</u>	<u>Nominal</u>	<u>High Flow</u>
Flow Rate	Q	Torr cm ³ /s	1x10 ⁻³	5x10 ⁻³	2.5x10 ⁻²
Source Conductance	c _s	cm ³ /s	1	50	250
Volume*	V	cm ³	0.1	1	1
Time Constant	τ	s	0.1	0.020	0.005
Source Sensitivity	S	A/Torr	2x10 ⁻⁷	2x10 ⁻⁶	2x10 ⁻⁶
Ion Current, Maximum	I _{max} ⁺	A	2x10 ⁻¹⁰	2x10 ⁻¹⁰	2x10 ⁻¹⁰
Source Pressure, Maximum	p _{max}	Torr	1x10 ⁻³	1x10 ⁻⁴	1x10 ⁻⁴
Background Pressure	p _{BG}	Torr	1x10 ⁻⁷	2x10 ⁻⁸	4x10 ⁻⁹
Pump Speed	S _p	ℓ/s	0.2	1	5
Differential Pumping Ratio	p _s /p _a		200	21	21

* Ionizing Region

The low flow design is a high pressure ion source designed for a particular application. The source sensitivity (S) in this case is limited by the small effective ionization region. Low source conductance is obtained by restricting the electron beam apertures and the ion exit slit resulting in low source sensitivity. The response time for this source is relatively long and since the source has a high surface-to-volume ratio and operates at high pressures, memory effects are enhanced and it would be of marginal utility for analysis of reactive species. The high differential pumping ratio, p_s/p_a , indicates that instrument background levels would contribute less than one percent to the sample measurement and that source pressure would be relatively unaffected by changes in pump speed.

For constant Q

$$\frac{dp_s}{p_s} = \frac{dS_p}{S_p} \left[\frac{S_p}{c_s} + 1 \right]^{-1}$$

and for

$$\frac{S_p}{c_s} + 1 = 200$$

and

$$\frac{dS_p}{S_p} = 10\%$$

$$\frac{dp_s}{p_s} = 0.05\%$$

This type of source could be used with a quadrupole analyzer for mass scan applications. It is doubtful that it could be employed with an electrostatic scanning instrument since the small source volume would not accommodate the additional electrodes.

The second column (nominal flow rate) shows the design parameters for the Mars Viking mass spectrometer for comparison. The source sensitivity is higher, and the response time faster, but the lower maximum

source pressure results in the same maximum ion current. In this case, the ion source pressure is limited by the source conductance and the pump speed. The source is designed to interface with a relatively (for flight instruments) high resolution analyzer. This is an overriding consideration in sizing the apertures in the source. Conductance is minimized within the constraints imposed by these design goals. The source pressure is more sensitive to changes in pump speed, and instrument background effects are slightly larger for this source.

The last column is typical of a so called "open" source. A faster pump is required to maintain the low analyzer pressure with the high flow rate into the source. System background is lower and sample surface interactions are minimized. This sort of design is frequently employed to analyze upper atmospheric samples containing species reactive at relatively low pressures.

Two general limitations on source and analyzer pressures are important considerations in instrument design. Space charge effects will result in nonlinear outputs for some source pressure which depends on the particular source design. For a given electron beam current, there will be a maximum source pressure for linear response operation. The other design limitation is on the analyzer pressure. At some pressure dependent on the particular analyzer design, collisions of the gas in the analyzer with the ion beam will result in loss of sensitivity. This limit is usually not approached in most system designs.

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